stirring in 25 min to a cold solution (-10 °C) of (2R,3R)-tartaric acid dimethyl ester (89.0 g, 0.5 mol) and triethylamine (8.9 g, 87.9 mmol) in dichloromethane (200 mL). The reaction mixture was stirred at -10 °C for 15 min and poured into a 5% HCl solution (200 mL). The aqueous phase was extracted with dichloromethane (200 mL). The combined organic extracts were washed with water (2 × 200 mL), dried over sodium sulfate, and concentrated under reduced pressure. A solid residue (14.3 g) was obtained, which was chromatographed on silica gel (diethyl ether/*n*-hexane = 3:7) to give pure **10j** (13.3 g, 34.0 mmol, 85% yield): mp 79-81 °C, $[\alpha]^{20}_D$ +72.4° (*c* 1, $CHCl_3$). According to the above procedure, **11j** was prepared starting from 2(*R*)-(6-methoxy-2-naphthyl)-propanoyl chloride.

A solution of bromine (0.43 g, 2.7 mmol) in 1,2-dichloroethane (2 mL) was added in 15 min with stirring at 0 °C to a solution of **10j** (1.01 g, 2.6 mmol) in 1,2-dichloroethane (10 mL). The reaction mixture was stirred at 0 °C for 45 min and poured into a 10% aqueous sodium carbonate solution (20 mL). The aqueous phase was extracted with dichloromethane (2 × 10 mL). The combined organic extracts were washed with a 5% aqueous solution of sodium thiosulfate (20 mL) and with water (20 mL). The organic phase was dried over sodium sulfate and the solvent was removed in vacuo to give a residue (1.14 g). Crystallization from methanol of the crude material afforded **10a** (1.04 g, 2.2 mmol, 85% yield): mp 123-125 °C; $[\alpha]^{20}_D$ +61.4° (*c* 1, $CHCl_3$); MS and ^{13}C and ^1H NMR data were found to be identical with those reported above.

Acknowledgment. We thank Mr. D. Tentorio for technical assistance and Prof. F. Minisci and Dr. S. Panossian for stimulating discussions.

Registry No. **1a** (isomer 1), 101154-44-3; **1a** (isomer 2), 101154-60-3; **1b**, 101154-49-8; **1c**, 101154-55-6; **1d**, 105785-45-3; **1e**, 100791-76-2; **1f**, 101154-61-4; **1g**, 100791-77-3; **1h**, 100791-78-4; **1i**, 101154-75-0; **2a**, 100791-79-5; **2b**, 101154-50-1; **2c**, 101154-56-7; **2d**, 107576-63-6; **2e**, 100791-83-1; **2f**, 101154-63-6; **2g**, 100791-85-3; **2h**, 100791-87-5; **2i**, 101154-76-1; **2j**, 101154-45-4; **3a**, 100791-80-8; **3b**, 101154-51-2; **3c**, 101154-57-8; **3d**, 107576-64-7; **3e**, 100791-84-2; **3f**, 101154-64-7; **3g**, 100791-86-4; **3h**, 100791-88-6; **3i**, 101154-77-2; **3j**, 101154-46-5; **8a**, 105817-50-3; **9a**, 105817-52-5; **10a**, 105926-81-6; **10b**, 105785-50-0; **10c**, 105879-58-1; **10d**, 105785-51-1; **10g**, 105785-52-2; **10h**, 105785-53-3; **10i**, 105857-33-8; **10j**, 101527-01-9; **11a**, 105785-48-6; **11b**, 105879-57-0; **11c**, 105785-49-7; **11d**, 105879-59-2; **11g**, 105879-60-5; **11h**, 105879-61-6; **11i**, 107741-22-0; **11j**, 101628-18-6; (*S*)-**17a**, 84236-26-0; (*R*)-**17a**, 92471-85-7; (*S*)-**17e**, 24470-14-2; (*R*)-**17e**, 4842-49-3; (*S*)-**17g**, 7782-24-3; (*R*)-**17g**, 7782-26-5; (*S*)-**17h**, 105879-63-8; (*R*)-**17h**, 105879-62-7; (*S*)-**17j**, 22204-53-1; (*R*)-**17j**, 23979-41-1; (*S*)-**18j**, 102849-62-7; (*R*)-**18j**, 107656-29-1; 1-(4-methoxyphenyl)propan-1-one, 121-97-1; (2*R*,3*R*)-tartaric acid dimethyl ester, 608-68-4; 1-phenylpropanone, 93-55-0; 1-(4-chlorophenyl)propan-1-one, 6285-05-8; 1-(4-chlorophenyl)-3-methylbutan-1-one, 71573-93-8; 2-acetyl-6-methoxynaphthalene, 3900-45-6; (2*S*,3*S*)-tartaric acid dimethyl ester, 13171-64-7; (2*R*,3*R*)-tartaric acid diisopropyl ester, 2217-15-4; (2*R*,3*R*)-tartaric acid dibutyl ester, 87-92-3; 1-(6-methoxy-2-naphthyl)propan-1-one, 2700-47-2; 2-methoxynaphthalene, 93-04-9; 2-bromo-1-(4-methoxyphenyl)propan-1-one, 21086-33-9; 2(*S*)-bromopropionyl chloride, 22592-73-0; 2(*S*)-(6-methoxy-2-naphthyl)propanoyl chloride, 51091-84-0; (2*R*,3*R*)-tartaric acid diethyl ester, 87-91-2; 1-[4-(2-methylpropyl)phenyl]propan-1-one, 59771-24-3; 1-butanol, 71-36-3; 2-bromo-6-methoxynaphthalene, 5111-65-9; acetic acid, 64-19-7.

Hydroxide-Initiated Gas-Phase Chemistry of Anthraquinone and Related Quinones

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Low-pressure gas-phase reactions of OH^-, $^{18}OH^-$, and OD^- with anthraquinone, naphthoquinone, benzoquinone, and various alkyl-substituted analogues have been characterized via Fourier transform mass spectrometry. The primary reactions are proton abstraction to yield M - H anions. In addition, anthraquinone, naphthoquinone, and benzoquinone produce abundant $(M + 17)^-$ ions. Ejection studies establish that these ions are formed from secondary reactions of $(M - H)^-$ with water and are represented as $[M - H + (H_2O)]^-$. The $(M - H)^-$ anions from anthraquinone and naphthoquinone react with their neutral precursors to produce anionic adducts, $(M - H + M)^-$, with *m/z* 415 and 315, respectively. Collision-activated dissociation confirms the structure of the adducts. Significant H/D exchange and oxygen-16/oxygen-18 exchange occurs when D_2O or $H_2{}^{18}O$ are present. The results are discussed in relation to the mechanisms that have been proposed for OH^-/quinone reactions in solution.

Introduction

Single-electron-transfer reactions, which result from the interaction of electron acceptors with electron donors, often are implicated in the mechanisms of heterolytic chemical reactions. There have been several reports[2,3] of anion radical formation from the interaction of bases and/or nucleophiles with a variety of organic electron acceptors. However, in many cases, the mechanisms by which such ions are generated remain unknown.

The various quinoid species (Q) react with OH^- in aqueous and nonaqueous solution to generate the corresponding semiquinone anion radicals ($Q^{\bullet -}$).[4,5] The redox chemistry of quinones has been well-documented in the condensed[6,7] and gas phase.[8] In view of these data, the reduction of Q by OH^- is intriguing because radical products are produced from nonradical reagents in a reaction that is thermodynamically disfavored (the redox potential for the $OH^-/OH^{\bullet}$ couple is +0.8 V vs. NHE in acetonitrile whereas that for most quinone/semiquinone

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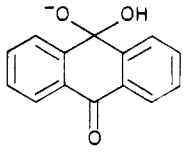
couples ($Q/Q^{\bullet-}$) is about −0.3 V).[6] Thus an outer-sphere electron transfer to generate free $Q^{\bullet-}$ and $OH^{\bullet}$ is precluded.

In a recent study[5] of the one-electron reduction of anthraquinone (AQ) by hydroxide ion in dipolar aprotic media, Roberts and co-workers have proposed an electron-transfer mechanism that involves an initial nucleophilic addition of OH^- at the carbonyl group of anthraquinone. The resulting intermediate (structure I) then



I

undergoes electron transfer with a second quinone to generate $AQ^{\bullet-}$. Nucleophilic addition of OH^- at the carbonyl carbon has been observed[9] for a variety of substituted 1,4-benzoquinones and quantitative formation of benzosemiquinone anion radical results from the reaction of 1,4-benzoquinone with hydroxide ion in dimethylformamide.[10] However, an alternative to nucleophilic addition to the carbonyl has been proposed[11] in which an initial proton transfer generates a quinone anion and water. The $(Q - H)^-$ anion then reduces a second quinone to produce a neutral and an anionic semiquinone radical.

The proposed involvement of the OH^-/quinone interaction with oxygen–oxygen bond formation in photosynthesis[12] and the commercial importance of this reaction in alkaline wood pulping[13] has prompted an investigation of the quinone/hydroxide system in the gas phase. In view of the importance of solvent effects in electron-transfer reactions, the gas-phase study provides a matrix-free reference point for the earlier solution studies and insight into the role of solvent in the condensed-phase reactions. Fourier transform mass spectrometry[14] (FTMS) offers a convenient way to study these systems at pressures of 10^{-8} and 10^{-7} Torr. Use of a trapped-ion cell allows the interactions of ions and neutrals to be observed after reaction periods that range from a few milliseconds to many seconds. Additionally, the variety of experimental techniques available with FTMS greatly facilitate the determination of ion structures and reaction pathways.

Experimental Section

Gas-phase reactions were studied with a Nicolet Analytical Instruments FTMS-1000 Fourier transform mass spectrometer equipped with a 2.54 × 2.54 × 7.62 cm^3 trapped-ion cell and a 3-T superconducting magnet. A 100-ms beam of −6.0 eV with a filament emission current of 1 μA was used to generate negative ions, which were retained in the cell by a −1-V trapping potential. All ions, except for hydroxide, were ejected from the cell by application of the appropriate radio frequencies (rf). A 4.6-MHz rf pulse, applied to the rear trap plate for 5 to 10 ms immediately after the electron-beam pulse, ejected electrons at their longitudinal oscillation frequencies. The ejection of electrons was essential; otherwise, despite ejection-rf sweeps, the molecular ion of the quinone (formed from electron capture of trapped electrons) was the only ion observed. The reactions of hydroxide ion with neutral quinones were monitored for reaction times between 5 ms and 15 s.

Two experimental sequences were utilized for ion-ejection studies. The first, which was used to determine the precursors of anionic products, applied a discrete rf continuously and monitored the disappearance of product ions from the spectrum. Another ion-ejection sequence was used to study the chemistry of the individual reaction products; OH^- and the quinone were allowed to react and one of the product ions was selected for reaction (by ejecting all other ions). Ions that reformed were assumed to result from interaction of the selected ion with neutrals. This reaction sequence provided data to confirm the results of the first ion-ejection sequence and the existence of secondary reactions.

In the collision-activated dissociation[15] (CAD) studies the parent ion was irradiated with a 100–300-μs rf pulse at its cyclotron resonance frequency and daughter ions were detected after a 100-ms collision time. Water and collision gas (argon) were maintained at 3.0×10^{-7} Torr and 1.44×10^{-6} Torr, respectively. The parent ion was formed during a 500–1000-ms reaction of the quinone and OH^- and isolated by ejection of the other product ions.

Water was used as the source of OH^- at a pressure of 2×10^{-7} Torr. The source of OD^- was D_2O (Aldrich, 98% D) at $2–6 \times 10^{-7}$ Torr, and $^{18}OH^-$ from $H_2{}^{18}O$ (Bio-Rad, 98% ^{18}O) at $2–4 \times 10^{-7}$ Torr. The $^{18}OH^-$ concentration was varied by incremental increases of the emission current from 85 nA to 1.6 μA while a constant H_2O pressure of 2.2×10^{-7} Torr was maintained. The pressure of $H_2{}^{18}O$ was varied from 1.1×10^{-7} to 1.6×10^{-7} Torr and the emission current was maintained at 1.1 μA. Anhydrous OH^- was prepared by a two-step reaction that utilized $O^{\bullet-}$ to abstract a hydrogen atom from either propylene[16] or *n*-heptane.[17] Oxygen and $^{18}O_2$ (Bio-Rad, 99.5% ^{18}O, 0.21% ^{17}O) were used as the sources of $O^{\bullet-}$ and $^{18}O^{\bullet-}$, respectively. A 100-ms, −5.5-eV electron beam with a 1-μA emission current produced large quantities of $O^{\bullet-}$, which was allowed to react with the hydrocarbon for about 100 ms to yield OH^-. Subsequently, unreacted $O^{\bullet-}$ and the other products of electron ionization were ejected.

Quinones were introduced via the volatile sample inlet (at 5×10^{-8} Torr or less) or a direct insertion probe. The exact pressure of the quinone when introduced via the direct insertion probe could not be determined because of the propensity of samples to adhere to the surfaces of the vacuum system, and, thereafter, to continuously outgas. If the sample was introduced via the probe, the ion gauge reading was allowed to drop below 2×10^{-8} Torr before experiments were initiated.

Most of the quinones and reagents were obtained from commercial sources (Aldrich), were the best grade available, and were used as received. 2,3,5-Trimethyl-1,4-benzoquinone was prepared by mercury(II) oxide oxidation of 2,3,5-trimethylhydroquinone (Aldrich) in methanol.[18] 2-(Methyl-d_3)-1,4-naphthoquinone was synthesized from 2-(methyl-d_3)naphthalene (95% pure) by oxidation with CrO_3 in glacial acetic acid.[19]

2-(Methyl-d_3)anthraquinone was synthesized from 2-methylanthracene. In a typical procedure 0.2 g (0.008 mol) of sodium hydride was added to 5 mL of 99.9 atom % deuteriated dry dimethyl sulfoxide (Aldrich) and 5 g (0.025 mol) of 2-methylanthracene. The slurry that resulted was heated at 110 °C for 24 h. On cooling, the solution was diluted with deuterium oxide and extracted with ether. The ether solution was dried over sodium sulfate and the solvent removed by rotary evaporation to yield the crude product. The exchange was repeated two more times to yield a product, which, on the basis of NMR analysis, contained >96% 2-(methyl-d_3)anthracene. The crude product was then oxidized to the corresponding quinone by ceric ammonium nitrate in tetrahydrofuran.[20]

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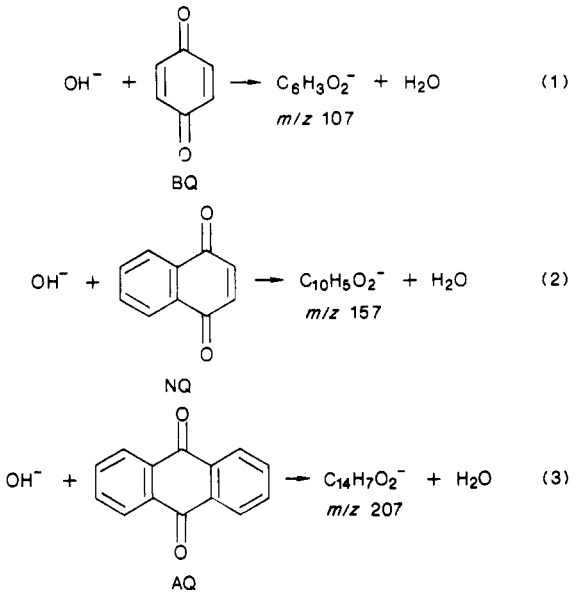
To a solution of 0.283 g (0.0015 mol) of 2-(methyl-d_3)anthracene in 12 mL of a 3:1 tetrahydrofuran/D_2O mixture was added 3.3 g (0.006 mol) of ceric ammonium nitrate, and the mixture was stirred at 25 °C for 10 min. TLC analysis at this stage (50:50 toluene/hexane on silica gel) confirmed complete conversion. After 10 mL of D_2O was added, the reaction mixture was extracted with dichloromethane. Evaporation of the dichloromethane extract gave a brown oil, which was purified by silica gel column chromatography. Removal of solvent gave a light-yellow solid [0.20 g (0.001 mol), 66.6% yield], which was further purified by vacuum sublimation to yield yellow crystals (>98% 2-(methyl-d_3)anthraquinone by NMR analysis).

Analysis by FTIR and GC/MS indicated that benzoquinone and methylbenzoquinone (which darkened on standing) contained minor impurities. A variety of methods for purification, including vacuum sublimation, produced bright yellow quinones; however, trace impurities, such as the 1,4-dihydroxy derivatives, were still present. This problem was alleviated by introduction of BQ through the volatile inlet system; reduction of BQ in the FTMS did not occur to a significant extent on the basis of periodic examination of its positive-ion spectrum.[21] The positive-ion mass spectrum of 1,4-benzoquinone exhibited a $(M + 2)^+$ ion whose intensity was less than 15% that of the M^+ ion.

Results

Unsubstituted Quinones. For reaction times shorter than 300 ms, the major gas-phase reaction products from the reaction of hydroxide ion with 1,4-benzoquinone (BQ), 1,4-naphthoquinone (NQ), and 9,10-anthraquinone (AQ) are the $(M - H)^-$ ions (eq 1–3). For longer reaction times



secondary products are produced which correspond to $(M + 17)^-$ for all three compounds and $(M - H + M)^-$ for NQ and AQ only.[22] (Figure 1 depicts the course of the gas-phase reaction of anthraquinone with hydroxide ion.) For the BQ system an ion with m/z 97 also is observed. An unresolved peak (19% relative abundance to $(M - H)^-$) composed of the ^{13}C satellite of $(M - H)^-$ (≈3/4) and the molecular anion ($M^{\bullet -}$, ≈1/4) is observed for all three systems. $M^{\bullet -}$ ions are produced even when hydroxide is continuously ejected and are the result of residual trapped electrons not removed by the supplementary ejections.

The relative abundances of $(M - 17)^-$ and $(M - H + M)^-$ are dependent upon the relative pressure of H_2O and neutral quinone. An increase in the pressure of water enhances formation of $(M + 17)^-$ over that of $(M - H + M)^-$. Following sample introduction via the solids probe,

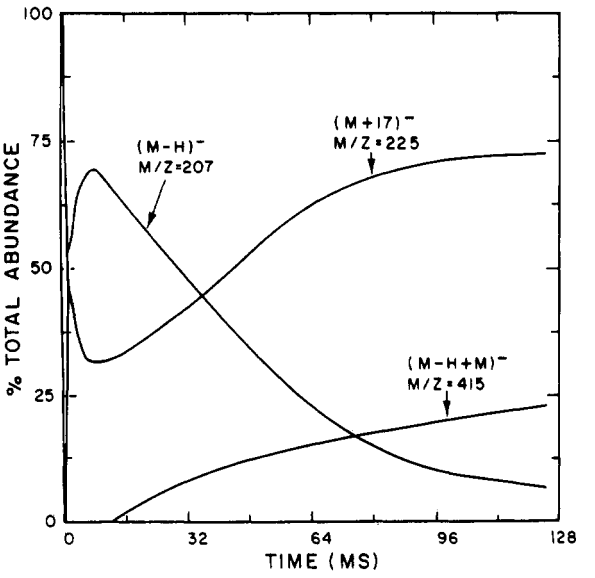


Figure 1. Normalized abundances of the product ions for the OH^-/H_2O/anthraquinone system, as a function of time. The primary product of the reaction is the $(M - H)^-$ ion. $(M - H)^-H_2O$ and $(M - H + M)^-$ are secondary products. This product distribution is for a 3.0×10^{-7} Torr pressure of H_2O with a 100 ms, 1 μA, −6.0 eV electron beam. The pressure of anthraquinone introduced via the solids probe was $<2 \times 10^{-8}$ Torr.

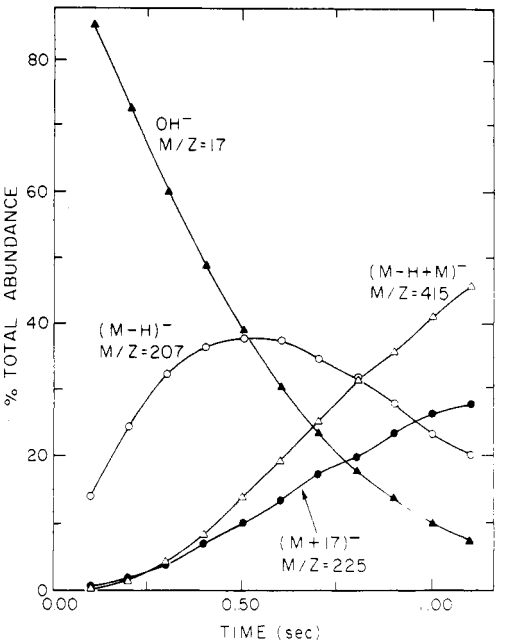


Figure 2. Normalized abundances of the product ions from the reaction of $(AQ - H)^-H_2O$ with neutrals as a function of time. $(AQ - H)^-H_2O$ rapidly decomposes to $(AQ - H)^-$; with increasing reaction times $(AQ - H)^-$ reacts with water to regenerate $(AQ - H)^-H_2O$ and reacts with anthraquinone to produce the adduct, $(AQ - H + AQ)^-$. The experimental conditions were similar to those used to obtain the data in Figure 1.

(21) Although 1,3-benzoquinones and 1,2-naphthoquinones can undergo reduction by residual water in the inlet systems of conventional mass spectrometers, 1,4-quinones are much more inert. (a) Ukai, S.; Hirose, K. *Tetrahedron Lett.* **1967**, 4999–5002. (b) Heiss, J.; Zeller, K.-P.; Reiker, A. *Org. Mass Spectrom.* **1969**, *3*, 1325–1334. (c) Das, B. C.; Lounasmaa, M.; Tendille, C.; Lederer, E. *Biochem. Biophys. Res. Commun.* **1965**, *21*, 318–322.

(22) For reaction times greater than 2 s, ions with m/z 215 appear. These ions are never more abundant than 2% of the major product [BQ − H + (H_2O)] and may be $(BQ - H + BQ)^-$, respectively. In addition, ions with m/z 143, 159, 161, 171, 187, and 205 are observed that may result from reactions of BQ with impurities. These ions are present in the negative-ion spectrum of BQ at pressures greater than 1×10^{-6} Torr and are enhanced by the presence of OH^-. Their abundance diminishes to almost zero when $(BQ - H)^-$ or $BQ^{\bullet -}$ are ejected. They do not result from the reactions of 1,4-dihydroxybenzene because in the OH^-/H_2O/1,4-dihydroxybenzene system only ions with m/z 109, $(M - H)^-$, and 219, $(M - H + M)^-$, are observed.

Table I. Hydrogen/Deuterium Exchange Data for $(M - H)^-$ Carbanions in the OD^-/D_2O/Quinone Systems

compound	M_r	relative abundance[a] $(M-H)^-$-d_0	$(M-H)^-$-d_1	$(M-H)^-$-d_2	$(M-H)^-$-d_3	$(M-H)^-$-d_4	$(M-H)^-$-d_5	$(M-H)^-$-d_6	$(M-H)^-$-d_7
benzoquinone	108		100	10[b]	17[b]	2[b]			
methylbenzoquinone	122	100	40	14[c]	37[c]	6[c]			
2,6-dimethylbenzoquinone	136	100	48	86[c]	8[c]	3[c]			
duroquinone	164	100	11	1					
2,6-di-*tert*-butylbenzoquinone	220	100	22	6	17[c]				
naphthoquinone[d]	158	24	100	41	28	21	12		
anthraquinone[e]	208	25	23	21	23	19	29	42	100
2-methylanthraquinone	222	100	58	24	21	15	3		
2-ethylanthraquinone	236	100	67	29	20	14			
2-*tert*-butylanthraquinone	264	74	88	100	95	57	37	24	11

[a] For a 1-s reaction time. Ion abundances are not corrected for contributions due to the ^{13}C isotope. [b] May be the result of 1,4-hydroquinone; especially the $(M + H)^-$-d_4 because $(BQ - H)^-$ only has 3 hydrogen atoms. [c] May be the result of the 1,4-dihydroxybenzene contaminent. [d] The deuterium incorporation in $(M + 17)^-$ and $(M - H + M)^-$ ions followed the $(M - H)^-$ ion. For the $(M + 17)^-$ and $(M - H + M)$ ions a maximum of 5 deuteriums were incorporated and $(M + 17)^-$-d_3 and $(M - H + M)^-$-d_1 were the most abundant anions. [e] For a 500-ms reaction time. The deuterium incorporation in $(M + 17)^-$ and $(M - H + M)^-$ followed $(M - H)^-$ with a maximum of seven deuteriums incorporated by each ion.

the pressure of quinone decreases, and the ratio of $(M + 17)^-$ to $(M - H + M)^-$ increases. The reaction of anhydrous hydroxide yields $(M - H)^-$ for BQ, NQ, and AQ and $(M - H + M)^-$ for NQ and AQ; under these conditions $(M + 17)^-$ ions are not produced.

Ion-ejection studies establish that the $(M - H)^-$ carbanion is the direct precursor of the $(M + 17)^-$ and $(M - H + M)^-$ ions. When $(AQ + 17)^-$ is the only ion retained for reaction, $(AQ - H)^-$ reforms. Figure 2 illustrates the decomposition of $(AQ + 17)^-$ to $(AQ - H)^-$ and the subsequent reactions of $(AQ - H)^-$ to produce $(AQ + 17)^-$ and $(AQ - H + AQ)^-$. In contrast, only 5% of the $(NQ + 17)^-$ ions decompose to $(M - H)^{\bullet -}$, the $(BQ + 17)^-$ ion is even more stable.

Collision activated dissociation (CAD) of $(AQ - H + AQ)^-$, m/z 415, yields three daughter ions with m/z 179, 207, and 208 (Figure 3). Application of a 6.6-eV rf pulse, corresponding to a maximum translational energy of 19.6 eV for m/z 415 at 3 T, produces an m/z 207 ion (eq 4).

$$(AQ\text{-}H + AQ)^-_{m/z\ 415} \xrightarrow{CAD} (AQ\text{-}H)^-_{m/z\ 207} + AQ \quad (4)$$

$$(AQ\text{-}H + AQ)^-_{m/z\ 415} \xrightarrow{CAD} C_{13}H_7O^-_{m/z\ 179} + CO + AQ \quad (5)$$

$$(AQ\text{-}H + AQ)^-_{m/z\ 415} \xrightarrow{CAD} AQ^-_{m/z\ 208} + (AQ\text{-}H)^{\bullet} \quad (6)$$

As rf energy is increased daughter ions with m/z 179 and 208 (eq 5 and 6) are produced. Collision-activated dissociation of $(AQ - H)^-$, m/z 207, also yields a daughter ion with m/z 179, eq 7. Off-resonance CAD of the $(M + 17)^-$

$$C_{14}H_7O_2^-_{m/z\ 207} \xrightarrow{CAD} C_{13}H_7O^-_{m/z\ 179} + CO \quad (7)$$

ions for AQ yields a daughter ion with m/z 207. No products are observed from CAD of $(M + 17)^-$ from NQ or BQ.

The results of hydrogen/deuterium (H/D) exchange[23-25] in the presence of OD^- and D_2O for the AQ, NQ, and BQ systems are summarized in Table I. Continuous ejection of individual ions in the $(AQ - H)^-$-d_0-d_7 series and $(NQ - H)^-$-d_0-d_7 series, or of the $(M + 17)^-$ ions does not stop H/D exchange. However, the corresponding deuteriated "dimer" $(M - H + M)^-$ ion is no longer observed.

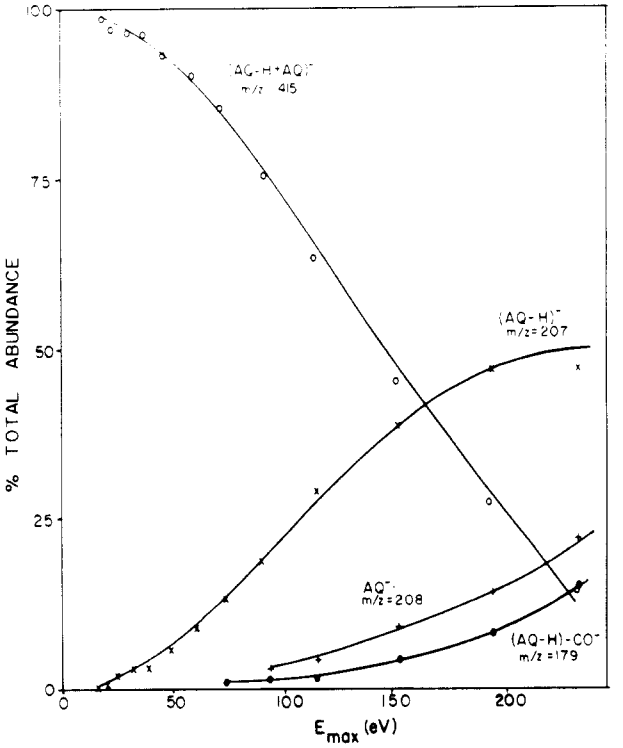


Figure 3. Variation of the relative CAD product-ion abundances as a function of maximum collision energy for the m/z 415 ion, $(AQ - H + AQ)^-$. The initial daughter ion is $(M - H)^-$ with m/z 207. As the translational energy of the parent ion is increased, loss of CO from $(AQ - H)^-$ produces an ion with m/z 179. The ion with m/z 208 ($M^{\bullet -}$) may be from charge exchange or from CAD.

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Table II. Oxygen-16/Oxygen-18 Exchange Data for the (M - H)⁻ Carbanions in the $^{18}OH^-/H_2{}^{18}O$/Quinone Systems

compound	reactn time, s	relative abundance 0-^{18}O	1-^{18}O	2-^{18}O
benzoquinone[a,b]	2	100		
methylbenzoquinone	5	100		
1,6-dimethylbenzoquinone	5	100		
trimethylbenzoquinone	5	100	4	
duroquinone	5	100	5	
naphthoquinone[c]	8	6	100	
anthraquinone[d]	0.8	12	48	100
2-methylanthraquinone	4	100	28	2
2-ethylanthraquinone	5	100	29	2

[a] An ion with m/z 109 appears; however, it has almost the same relative intensity, 11%, as in the OH^-/H_2O/BQ system and therefore is the result of proton abstraction from 1,4-dihydroxybenzene. If $^{16}O/^{18}O$ exchange does occur it is very slow. [b] One ^{18}O is incorporated by $(M - H)H_2{}^{18}O$ from $H_2{}^{18}O$. [c] Two ^{18}O are incorporated by $[(NQ - H)H_2{}^{18}O]^-$ (one is from $H_2{}^{18}O$) and one ^{18}O is incorporated by $(NQ - H + NQ)^-$. [d] Three ^{18}O's are incorporated by $[(AQ - H)H_2{}^{18}O]^-$ (one is from $H_2{}^{18}O$) and two ^{18}O are incorporated by $(AQ - H - AQ)^-$.

In the presence of $H_2{}^{18}O$ all products for the AQ and NQ systems (but not for the BQ system) incorporate ^{18}O (see Table II). Ion ejection studies indicate that the primary ions, $(AQ-H)^-$ and $(NQ - H)^-$, rather than $^{18}OH^-$, are the ionic precursors of $^{16}O/^{18}O$ exchange. This is confirmed by the observation that when anhydrous $^{18}OH^-$ is used, no $^{16}O/^{18}O$ exchange is observed for $(NQ - H)^-$ and only 10–22% of the $(AQ - H)^-$ ions incorporate one ^{18}O (it cannot be determined if ^{18}O incorporation in the anhydrous $^{18}OH^-$ experiment is due to $^{18}O^{\bullet-}$, $^{18}O_2$, $^{18}OH^-$, or residual $H_2{}^{18}O$).

Alkyl-Substituted Quinones. As with the unsubstituted quinones, the primary products from the reaction of hydroxide ion with alkyl-substituted benzoquinones, naphthoquinones, and anthraquinones are the corresponding M - H carbanions (eq 8). However, differences

$$OH^- + M \rightarrow (M - H)^- + H_2O \quad (8)$$

M = methylbenzoquinone, 2,6-dimethylbenzoquinone, trimethylbenzoquinone, duroquinone, 2-methylnaphthoquinone, 2-methylanthraquinone, 2-ethylanthraquinone, 2-*tert*-butylanthraquinone, and α-tocopherol quinone

are observed for alkyl-substituted derivatives in both the site and degree of deuterium exchange and the rate of ^{18}O incorporation. Reaction of OH^- with 2-(methyl-d_3)-naphthoquinone and 2-(methyl-d_3)anthraquinone produces abundant $(M - D)^-$ ions; the ions from aryl hydrogen abstraction are less abundant (Table III). Secondary products, $(M + 17)^-$ and $(M - H + M)^-$, total less than 1% of the ionic products with the exceptions of 2-methylnaphthoquinone, methylbenzoquinone, 2,6-dimethylbenzoquinone, and trimethylbenzoquinone.[31]

In the presence of D_2O, less H/D exchange occurs than for the unsubstituted anthraquinones and naphthoquinones. Table I also indicates that the alkylanthraquinones and 2-methylnaphthoquinone (MeNQ) exhibit more H/D exchange than methyl-substituted benzoquinones. Comparison of H/D exchange data for $(MeNQ\text{-}d_3 - D)^-$ and $(MeAQ\text{-}d_3 - D)$ in the presence of OH^-/H_2O and OD^-/D_2O (Table III) confirms that in addition to exchange of alkyl hydrogens, exchange of aryl hydrogens also occurs for these systems (additional exchange probably occurs but is too slow to be observed under the experimental conditions).

In the presence of $^{18}OH^-/H_2{}^{18}O$ alkyl-substituted quinones behave differently than naphthoquinone and anthraquinone. The $(M - H)^-$ ions of alkyl-substituted anthraquinones incorporate two ^{18}O atoms. However, unlike $(AQ - H)^-$, the M–H carbanion exchange is not so rapid that it reaches completion. Methyl-substituted benzoquinones incorporate ^{18}O slowly. For example, for duraquinone (after 5 s), the m/z 166 ion is only 5% of the unexchanged $(M - H)^-$ (m/z 164); it is too abundant to be a molecular ion of a $^{13}C_2$ species and, therefore, must be the result of $^{16}O/^{18}O$ exchange.

Mixed Adduct Formation. The results summarized in Table IV indicate that BQ does not undergo significant adduct formation with $(BQ - H)^-$ but forms adducts with other quinones. Ejection studies establish that the M - H carbanions from other quinones react with neutral BQ to form adducts. The ratio of the mixed adduct $(M - H + BQ)^-$ to the $(M - H + M)^-$ adduct is dependent upon the relative concentrations of the neutral quinones.

Discussion and Conclusions

Three primary reaction pathways are possible for the gas-phase interaction of quinone with hydroxide ion: proton abstraction, charge transfer, and nucleophilic addition. Proton abstraction is the primary process for all of the quinones studied. $(M + 17)^-$ and $(M - H + M)^-$ are formed by secondary reactions of $(M - H)^-$ with water (eq 9) and with neutral quinone (eq 10).

$$(M - H)^- + H_2O \rightarrow [M - H + (H_2O)]^- \quad (9)$$

$$M = C_6H_4O_2,\ C_{10}H_6O_2,\ C_{14}H_8O_2$$

$$(M - H)^- + M \rightarrow [M - H + M]^- \quad (10)$$

$$M = C_{10}H_6O_2,\ C_{14}H_8O_2$$

The structures of the conjugate bases of the alkyl-substituted quinones differ from those derived from AQ, NQ, and BQ, because proton abstraction of the more acidic alkyl hydrogens is favored relative to the aromatic or quinone ring hydrogens. The RCH_2^- carbanions from proton abstraction at the alkyl sites of substituted benzoquinones, naphthoquinones, and anthraquinones produce more stable anions as the result of inductive effects and resonance stabilization. The differences in the structures of the $(M - H)^-$ carbanions are responsible for the variation in their reactivities.

Formation and Structure of $(M + 17)^-$ Carbanions. The conclusion that the $(M + 17)^-$ species results from an H_2O adduct of $(M - H)^-$, i.e., $[M - H + (H_2O)]^-$ is supported by the observations that (a) $[M - H + (H_2O)]^-$ is not formed when anhydrous hydroxide is used as a reagent; (b) the abundance of $[M - H + (H_2O)]^-$ is enhanced by an increase in the pressure of H_2O; (c) an $[M - H + (H_2{}^{18}O)]^-$ ion is produced when $H_2{}^{18}O$ is present; (d) an $(M + 19)^-$ ion is produced when D_2O is the reagent; (e) $[M - H + (H_2O)]^-$ is absent if $(M - H)^-$ is ejected; and (f) $[M - H + (H_2O)]^-$ appears when $(M - H)^-$ reacts with neutrals. The fact that the $[M - H + (H_2O)]^-$ ion results from an H_2O adduct of $(M - H)^-$ is surprising because formation of such ions by nonreactive collisions in the 10^{-8}–10^{-4} Torr pressure range is rare. Nevertheless, methanol and *tert*-butyl alcohol form adduct ions with their respective conjugate bases.[26] The $[AQ - H + (H_2O)]^-$ anions in the present study result from nonreactive H_2O addition and decompose

(31) For 2-methylnaphthoquinone and methylbenzoquinone, the relative abundance of $(M + 17)^-$ is 8% and 20%, respectively. For reaction times greater than 5 s, the relative abundance of $(M - H + M)^-$ is 10% for 2-methylnaphthoquinone, methylbenzoquinone, and 2,6-dimethylbenzoquinone and 5% for trimethylbenzoquinone.

Table III. Comparison of Hydrogen/Deuterium Exchange for the OH^-/H_2O and OD^-/D_2O Systems of 2-(Methyl-d_3)naphthoquinone and 2-(Methyl-d_3)anthraquinone

compound	system	reactn time, s	no. of additional deuteriums incorporated in $(M - D)^-$ (total $(M - D)^-$ abundance)									
			-1	0	1	2	3	4	5	6	7	8
2-(methyl-d_3)naphthoquinone	OH^-/H_2O	4	5	54	24	11	4	1	0.3			
	OD^-/D_2O	4	2	19	29	19	16	10	3	0.7	0.3	0.3
2-(methyl-d_3)anthraquinone	OH^-/H_2O	2	2	71	8	15	4	0.4				
	OD^-/D_2O	2	1	39	18	26	10	5	1			

Table IV. Mixed Adduct, $(M - H + M')$, Formation in the OH^-/H_2O/Quinone Systems[a]

neutral quinone[b]		mixed product adducts obsd	carbanion, $(M - H)^-$, responsible for the mixed adduct[c]
A	B		
BQ	BQ	NR[d]	
BQ	NQ	m/z 265, $(NQ - H + BQ)^-$	$(NQ - H)^-$
BQ	AQ	m/z 315, $(AQ - H + BQ)^-$	$(AQ - H)^-$
BQ	MeBQ	m/z 229, $(MeBQ - H + BQ)^-$	$(MeBQ - H)^-$
NQ	AQ	m/z 364, $(AQ - H + NQ)^-$	$(AQ - H)^-$

[a] Quinone A was introduced via the volatile inlet and quinone B was introduced via the solids probe: therefore the relative concentrations of the two quinones are not known. [b] The quinones are designated as follows: BQ = benzoquinone; NQ = naphthoquinone; AQ = anthraquinone; and MeBQ = methylbenzoquinone. [c] The carbanion responsible for formation of $(M - H + M')^-$ was determined by continuous ejection of either $(M - H)^-$ or $(M' - H)^-$. [d] At reaction times greater than 2 s, an ion with m/z 215 (comprising <2% of the total product distribution) is observed which may correspond to $(BQ - H + BQ)^-$.

to reform reactants. The collision-activated dissociation results indicate that the $[M - H + (H_2O)]^-$ ions have low binding energies and readily decompose with the application of minimal rf energy. Because the $[AQ - H + (H_2O)]^-$ ions readily decompose to $(AQ - H)^-$, but only about 5% of the $[NQ - H + (H_2O)]^-$ ions and none of the $[BQ - H + (H_2O)]^-$ ions decompose to $(M - H)^-$, the relative binding energies of these H_2O adduct ions are in the order $[AQ - H + (H_2O)]^- < [NQ - H + (H_2O)] < [BQ - H]$. The reappearance of $^{18}OH^-$ during the ion ejection studies in which $(AQ - H)^-$ ions are isolated for reaction with neutral compounds indicates that the gas-phase acidities of AQ and H_2O may be close. The conjugate bases of the alkyl-substituted quinones are weaker bases, as a result of charge delocalizaton, than those of AQ, NQ, and BQ and are thus unable to form stable water adducts.

$(M - H + M)^-$ Carbanion. Formation of the $(M - H + M)^-$ anion from the reaction of $(M - H)^-$ with neutral quinones is supported by the following observations: (a) $(M - H + M)^-$ does not form when $(M - H)^-$ is continuously ejected during reaction; (b) $(M - H + M)^-$ is formed when $(M - H)^-$ is selected for reaction; (c) in the presence of OD^-/D_2O a maximum of seven deuterium atoms are incorporated by $(AQ - H + AQ)^-$ and five deuterium atoms by $(NQ - H + NQ)^-$; (d) in the presence of $^{18}OH^-/H_2{}^{18}O$ a maximum of two ^{18}O are incorporated by $(AQ - H + AQ)^-$ and one ^{18}O by $(NQ - H + NQ)^-$ (incorporation of D and ^{18}O in $(M - H + M)^-$ of the alkyl-substituted quinones also is similar to their respective $(M - H)^-$ carbanions); (e) CAD of $(AQ - H + AQ)^-$ yields $(AQ - H)^-$.

These studies indicate that the primary daughter ion produced by CAD of $(AQ - H + AQ)^-$ is $(AQ - H)^-$, while the other two ions produced with m/z 179, $(AQ - H - CO)^-$, and m/z 208, $(AQ^{\bullet-})$, result from secondary processes. As the energy of the rf excitation is increased the energy of $(AQ - H)^-$ increases with expulsion of CO. This mechanism is supported by CAD of $(AQ - H)^-$ for which expulsion of CO and formation of a daughter ion with m/z 179 also is observed; a similar loss of CO is noted for the

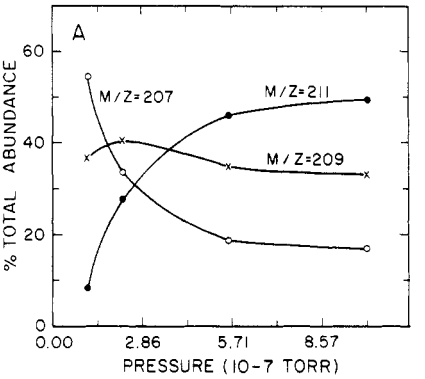
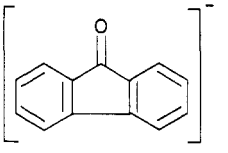


Figure 4. Effect of increased partial pressure of $H_2{}^{18}O$ on $^{16}O/^{18}O$ exchange in $(Aq - H)^-$. Constant emission current of 1.1 μA and a reaction time of 300 ms was used in each case.

CAD of the conjugate base of methylbenzoquinone. The structure of the m/z 179 ion probably corresponds to deprotonated fluorenone (structure II). It is interesting to



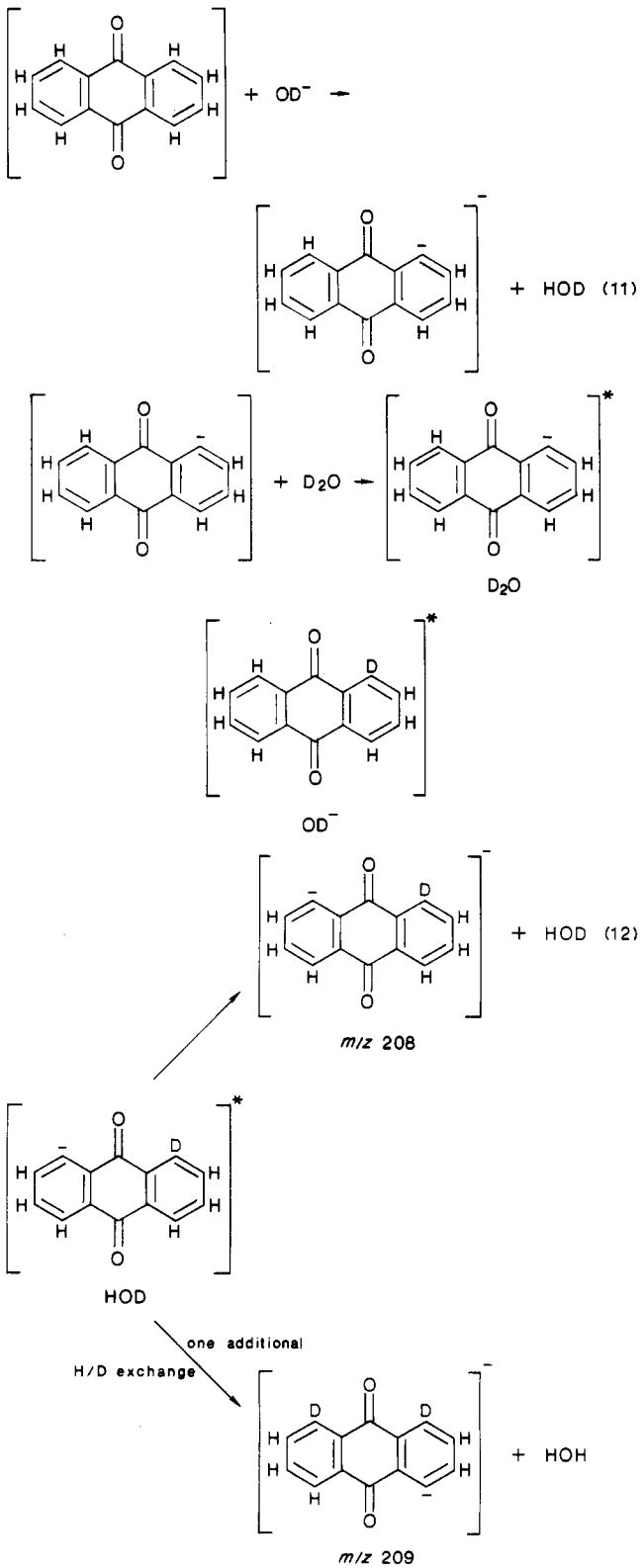
II

note that the positive-ion spectra of AQ and other quinones are distinguished by successive loss of CO from $M^{\bullet+}$. $(NQ - H + NQ)^-$ does not undergo CAD, indicating that the bond energy of this adduct is stronger than for $(AQ - H + AQ)^-$.

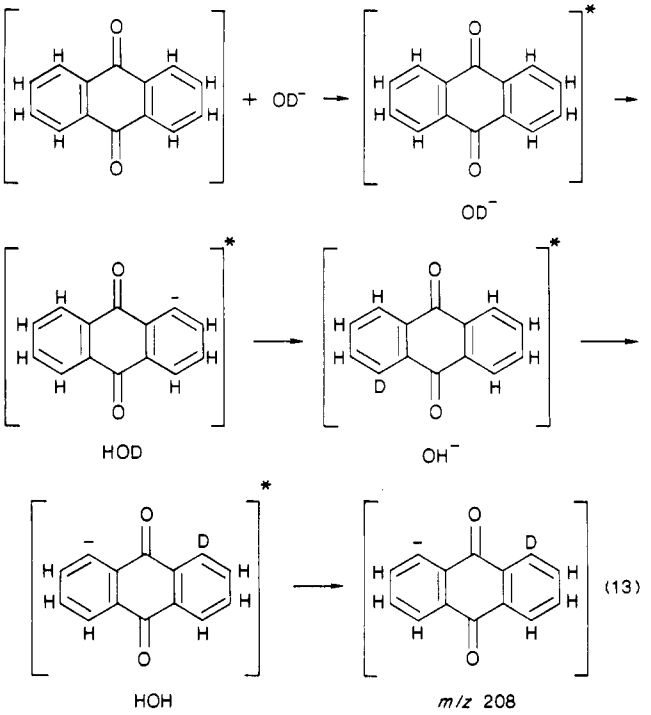
The tendency of AQ and NQ in the gas phase to form adducts with their $(M - H)^-$ ions (compared with minimal adduct formation for alkyl-substituted quinones) confirms that the negative charge on the aromatic ring favors adduct formation. Only low abundances of $(M - H + M)^-$ in the alkyl-substituted quinone systems are observed because proton abstraction at aryl sites is much slower than at alkyl sites. Neutral BQ readily forms adducts with $(M - H)^-$ carbanions other than $(BQ - H)^-$; repulsion of the oxygens may hinder formation of an adduct between BQ and $(BQ - H)^-$. The $(M-H+M)^-$ ions are either cluster ions that share a hydrogen atom between the two molecules or they result from nucleophilic attack of the $(M - H)^-$ carbanion upon a carbonyl carbon.

Hydrogen/Deuterium Exchange. In the presence of D_2O, $(AQ - H)^-$ exchanges all of its hydrogens at essentially the same rate, establishing that they have similar acidities. In contrast, the exchange data for $(NQ - H)^-$ indicate that one hydrogen is more acidic than the other four, suggesting that $(NQ - H)^-$ is formed by more rapid proton abstraction from the quinone ring rather than the aromatic ring. Comparison of the reaction profiles for 2-(methyl-d_3)-naphthoquinone with D_2O and H_2O (Table III) demonstrates that exchange of the aryl hydrogens occurs, but at a much slower rate than the alkyl exchange. Although the $(M - H)^-$ ion is the most likely to undergo H/D exchange with D_2O,[23-25] continuous ejection of $(M - H)^-$-d_0 and other

ions within the $(AQ - H)^-$-d_1–d_7 and $(NQ - H)^-$-d_1–d_5 series does not stop H/D exchange. Thus, two mechanisms must exist for the exchange process. In the first, exchange occurs via proton abstraction by OD^- from AQ to form $(AQ - H)^-$ (eq 11), which upon collision with D_2O undergoes one or

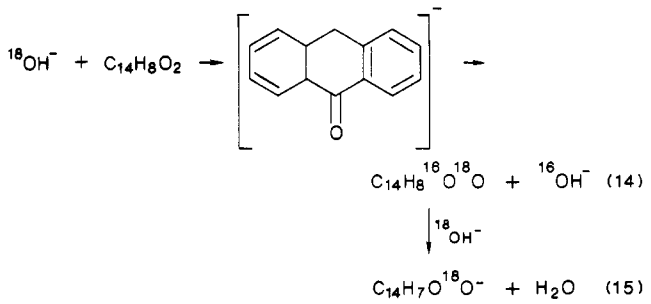


(if the reaction intermediate has a sufficiently long lifetime) two H/D exchanges (eq 12) before dissociation of the complex. Multiple exchange of hydrogen atoms occurs when the exchanged $(AQ - H)^-$ ions encounter another D_2O molecule; ejection of the $(AQ - H)^-$ ion prevents this exchange. The second exchange mechanism involves the initial ion/molecule complex of OD^- and AQ (eq 13). One



H/D exchange can occur by this pathway with additional H/D exchange via eq 12. The deuteriated $(AQ - H)^-$ ions that result despite continuous ejection of $(M - H)^-$-d_0 are formed in this manner. The activated complexes of eq 12 and 13 can revert to initial reactants; however, little or no dissociation to form $C_{14}H_7DO_2$ and OH^- occurs, because a maximum of seven deuteriums are incorporated by the $(AQ - H + AQ)^-$ anions.

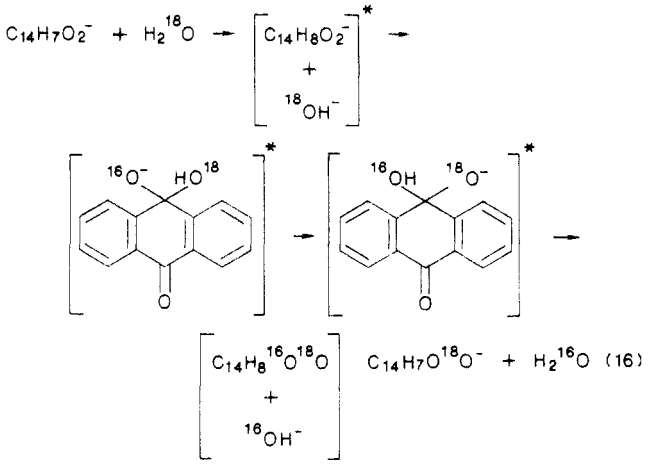
Oxygen-16/Oxygen-18 Exchange. Possible mechanism for $^{16}O/^{18}O$ exchange include attack by $^{18}OH^-$ at the carbonyl carbon[27] of the neutral quinone and exchange between $(M - H)^-$ and $H_2{}^{18}O$. The first mechanism, nucleophilic attack by $^{18}OH^-$ at the carbonyl carbon of neutral anthraquinone (eq 14) followed by deprotonation of ^{18}O-



anthraquinone (eq 15) is ruled out on the basis of ion injection studies in which $^{16}O/^{18}O$ exchange is greatly diminished (the exchange that is observed may result from reaction of $^{18}O_2$ with $(AQ - H)^-$, or from reaction of $^{18}O^-$ with AQ rather than $^{18}OH^-$). Oxygen-16/oxygen-18 exchange for compounds that contain carbonyl functional groups is often cited as evidence for formation of a tetrahedral intermediate.[27] However, the $(AQ + 17)^-$ ion is not the reaction intermediate for the exchange because its continuous ejection does not prevent $^{16}O/^{18}O$ exchange or formation of $(AQ - H)^-$.

For the second $^{16}O/^{18}O$ exchange mechanism, $(AQ - H)^-$ undergoes exchange with neutral $H_2{}^{18}O$, in which the first step involves proton abstraction from $H_2{}^{18}O$ by $(M - H)^-$. Nucleophilic addition to the carbonyl by $^{18}OH^-$ within the collision complex, followed by intramolecular proton

transfer, expulsion of OH^-, final proton abstraction, and loss of $H_2{}^{16}O$ (eq 16) yields $C_{14}H_7{}^{16}O^{18}O^-$. This $^{16}O/^{18}O$



exchange mechanism for compounds that contain carbonyl functional groups has not been documented previously. The presence of aromatic rings apparently stabilizes the intermediate, and exchange occurs more rapidly for $(AQ - H)^-$ than for $(NQ - H)^-$ with its single aromatic ring. This mechanism for $^{16}O/^{18}O$ exchange is supported by the observation that an increase in the $H_2{}^{18}O$ pressure enhances exchange (Figure 4).

In summary, the major reaction pathway for the quinone–hydroxide ion interaction in the gas phase is proton transfer to form the quinone carbanion and water. Such a reaction pathway is consistent with both the strong base properties and high electron affinity of unsolvated hydroxide ion in the gas phase. Less basic anions, with lower electron affinities than hydroxide, such as $O_2^{\bullet-}$, $O^{\bullet-}$, and t-BuO^- are expected to undergo electron transfer rather than proton transfer. For example, $O_2^{\bullet-}$ reacts to produce abundant molecular ions of $AQ^{\bullet-}$, $BQ^{\bullet-}$, and $NQ^{\bullet-}$, analogous to reactions in solution.

The predominance of electron transfer between OH^- and Q in solution is consistent with lowering the basic properties of OH^- by solvation. However, the inability of the quinone carbanion $(M - H)^-$ to undergo electron transfer with neutral quinone in the gas phase renders this mechanism even less likely in solution phase. The alternative solution-phase electron-transfer mechanism via nucleophilic attack of OH^- at the carbonyl carbon cannot be excluded on the basis of the gas-phase data. Such nucleophilic addition–elimination reactions at carbonyl centers are most favored when the intermediate complex is tetrahedral and stabilized by the solvent.

At higher pressures adducts can be observed in the gas phase when collisions are stabilized with a buffer gas.[27a,28] Although the results of many gas-phase nucleophilic displacement studies indicate that most intermediates are loose association complexes,[28] some reports indicate the formation of a tetrahedral intermediate.[27-30] Further work is planned to study the effects of increased pressure on the gas-phase reaction pathway. A correlation will be sought between the abundance of $M^{\bullet-}$ and the reaction pressure, and any new intermediates that result will be further characterized.

Acknowledgment. This work was supported by the National Institutes of Health under Grant GM-30604 (C.L.W.) and the National Science Foundation under Grants CHE-80-18245 and CHE-85-19087 (C.L.W.) and CHE-85-16247 (D.T.S.). C.L.J. gratefully acknowledges the support of the Shell Foundation Graduate Fellowship in Analytical Chemistry.

Registry No. *p*-Benzoquinone, 106-51-4; 2-methyl-*p*-benzoquinone, 553-97-9; 2,6-dimethyl-*p*-benzoquinone, 527-61-7; duroquinone, 527-17-3; 2,6-di-*tert*-butyl-*p*-benzoquinone, 719-22-2; 1,4-naphthoquinone, 130-15-4; 9,10-anthraquinone, 84-65-1; 2-methyl-9,10-anthraquinone, 84-54-8; 2-ethyl-9,10-anthraquinone, 84-51-5; 2-*tert*-butyl-9,10-anthraquinone, 84-47-9; 2,3,5-trimethyl-*p*-benzoquinone, 935-92-2; 2-(methyl-d_3)-1,4-naphthoquinone, 5172-16-7; hydroxide, 14280-30-9.