perimental conditions employed,[16] our data (Table I) would dictate virtually no inhibition. The finding, where *extensive inhibition* was observed (greater than 60%), further supports the proposition that the lipase-like activity of the "abzyme" is not a consequence of contamination. In addition, the antibody (20 μM) shows minimal inactivation (less than 20% when **2** is 400 μM) in the presence of the powerful acetylcholinesterase inhibitor diisopropyl phosphorofluoridate (DFP) (50 μM).[17]

Enantioselectivity of the antibody-catalyzed reaction was investigated by GC analysis of a large-scale reaction of 37E8 (40 μM) in ATE (ACES, Tris, ethanolamine), pH 8.0, containing 200 μM **1**. At selected time intervals an aliquot of the reaction mixture was removed (600 μL), extracted twice with a 50/50 mixture of ethyl ether/ethyl acetate, and injected onto a microcapillary gas chromatographic column (Chrompack, CP-(optically pure)-cyclodextran-B-236-M-19). At 8 h, 60 μM **2** was detected with enantioselectivity in excess of 86% for the (1*R*,4*S*)-(+)-4-hydroxy-2-cyclopentenyl acetate (**2**). After 14 h, 100 μM **2** with an ee of 84% was detected. These results, while gratifying, appear to be limited only by the catalytic activity of abzyme 37E8 rather than by an inherent lack of enantiotopic group differentiation.

A comparison of abzyme 37E8 to acetyl- and butyrylcholinesterase (Table I) provided us with a crude index for an abzyme–enzyme comparison. Moreover, it provides us with alternative methods to check antibody purity. A comparison of k_{cat} (Table I) shows abzyme 37E8 to be some 3–4 orders of magnitude less potent catalytically than the cholinesterases. However, the inherent enantio group selectivity of 37E8 is excellent (>98% ee).[18]

The abzyme obtained here is admittedly somewhat primitive compared to its enzymatic counterparts. However, these findings suggest that asymmetric synthesis with catalytic antibodies could well provide attractive opportunities in organic synthesis. Further applications along these lines are envisioned.

(16) The following experiment was performed: Catalytic antibody 37E8 (10 μM) was added to a solution of 800 μM **1** and 25 μM **3**. These conditions were chosen so that the concentration of substrate would be at saturation for the antibody ($4.5K_m$) and approximately K_m for either cholinesterase.

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(18) Calculated values, which was approximated by correcting for the unwanted antipode (1*S*,4*R*)-(−)-4-hydroxy-2-cyclopentyl acetate, which came from the competing background hydrolytic reaction.

Quinone/Hydroxide Ion Induced Oxygenation of *p*-Benzoquinone to Rhodizonate Dianion ($C_6O_6^{2-}$) Accompanied by One-Electron Reduction to Semiquinone Radical Anion

Shunichi Fukuzumi* and Tomohiro Yorisue

Department of Applied Chemistry, Faculty of Engineering Osaka University, Suita, Osaka 565, Japan

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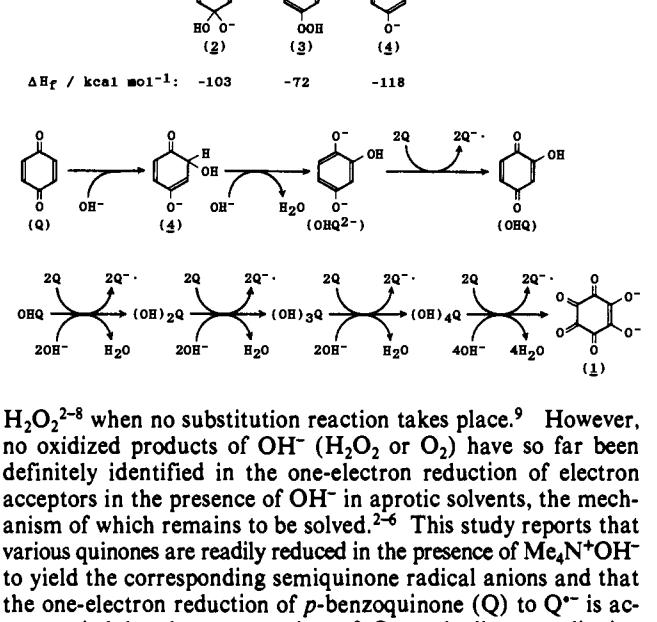
Hydroxide ion is regarded as a better electron donor as well as a stronger base in an aprotic solvent such as acetonitrile than in water, since the solvation energy for OH^- in an aprotic solvent is much less than in water.[1,2] Thus, OH^- in aprotic solvents has been reported to act as an electron donor toward quinones and other electron acceptors, since the radical anions of electron acceptors are often formed in the presence of OH^- in aprotic solvents.[2-6] The oxidized species of OH^- has been presumed to be H_2O_2[2-8] when no substitution reaction takes place.[9] However, no oxidized products of OH^- (H_2O_2 or O_2) have so far been definitely identified in the one-electron reduction of electron acceptors in the presence of OH^- in aprotic solvents, the mechanism of which remains to be solved.[2-6] This study reports that various quinones are readily reduced in the presence of $Me_4N^+OH^-$ to yield the corresponding semiquinone radical anions and that the one-electron reduction of *p*-benzoquinone (Q) to $Q^{\bullet-}$ is accompanied by the oxygenation of Q to rhodizonate dianion ($C_6O_6^{2-}$), which is the 10-electron-oxidized species of Q.

Upon mixing of *p*-benzoquinone (Q) with $Me_4N^+OH^-$ in deaerated MeCN at 298 K, Q is readily reduced to $Q^{\bullet-}$ (λ_{max} = 422 nm), and the yield based on the amount of OH^- is 100%.[10] The $Q^{\bullet-}$ thus formed is very stable in deaerated MeCN at 298 K. Similarly, the reactions of various quinones with $Me_4N^+OH^-$ yield the corresponding semiquinone radical anions.[11] No oxidized products of OH^- (H_2O_2 or O_2) have, however, been formed in the one-electron reduction of Q in the presence of OH^- in deaerated MeCN.[12] No oxidized products derived from the solvent (e.g., succinonitrile)[13] have been detected, either.[14] Then, the question

Scheme I



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(12) When the product mixture of the reaction of Q (2.0×10^{-2} M) with $Me_4N^+OH^-$ (2.0×10^{-2} M) was treated with Ph_3P (1.0×10^{-2} M) in deaerated MeCN, no formation of $Ph_3P{=}O$ was detected. When H_2O_2 was added to the same solution, however, Ph_3P was converted to $Ph_3P{=}O$ quantitatively in 40 min. Thus, it is concluded that no H_2O_2 is formed in the reaction of Q with OH^- in MeCN. The products in the gas phase were also analyzed by GLC using a molecular sieve 13 X column with He gas carrier. No appreciable formation of O_2 has been detected, either.

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arises. What is really oxidized in the one-electron reduction of Q in the presence of OH^- in MeCN? Scrutiny of the detailed stoichiometry of the reaction revealed that a slight excess of OH^- is required to complete the reaction when a part of *p*-benzoquinone (ca. 10%) is found to be oxidized to rhodizonate dianion (**1**: λ_{max} = 483 nm),[15,16] which corresponds to the 10-electron-oxidized species of *p*-benzoquinone.[17] Under such conditions, the stoichiometry of the reaction is given by eq 1, where the one-electron reduction of 10 Q is accompanied by the 10-electron oxidation of one Q.

$$11Q + 12OH^- \longrightarrow 10Q^{\bullet-} + \underline{1} + 8H_2O \quad (1)$$

(**1**)

Rates of the formation of $Q^{\bullet-}$ obeyed pseudo-first-order kinetics under conditions wherein the quinone concentrations [Q] were maintained at more than a 10-fold excess of OH^-. The observed pseudo-first-order rate constants k_{obsd} of most quinones were independent of [Q]. In the case of 2,5-dimethyl-*p*-benzoquinone (Me_2Q) the k_{obsd} value increased with an increase in [Me_2Q] to reach a plateau value. Such a saturated dependence of k_{obsd} on the quinone concentration indicates that the formation of $Q^{\bullet-}$ may proceed via the initial formation of the OH^- adduct of Q, followed by the rate-determining unimolecular step.

There are three possible forms of the OH^- adduct of Q. The first is the OH^- adduct on the carbonyl carbon of Q (**2**); the second is that on the carbonyl oxygen (**3**); and the last one is that on the carbon next to the carbonyl group (**4**). The first one has so far been simply assumed to be formed.[1,18] Our MNDO calculation[19] revealed that OH^- adduct **4** is most stable, as shown in Scheme I.[20-22] Deprotonation of OH^- adduct **4** produces the corresponding hydroxyhydroquinone dianion (OHQ^{2-}), which is a stronger reductant than $Q^{\bullet-}$ and therefore can reduce two Q to two $Q^{\bullet-}$ to yield OHQ (Scheme I). Thus, substitution of one hydrogen of Q by OH, which corresponds to the two-electron oxidation of Q, results in the one-electron reduction of two Q to yield two $Q^{\bullet-}$. Consequently, successive substitutions by OH finally result in the formation of 10-electron-oxidized species **1**, accompanied by the one-electron reduction of 10 Q to yield $10Q^{\bullet-}$ (Scheme I). Such novel disproportionation of Q is responsible for the apparently quantitative formation of $Q^{\bullet-}$ (eq 1). The rate-determining step may be the deprotonation of **4**. In such a case, k_{obsd} may be independent of the quinone concentration when the formation constant of the OH^- adduct is large enough, in agreement with the experimental results.

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Supplementary Material Available: A table showing the yields of semiquinone radical anions derived from various quinones and a figure exhibiting relations of k_{obsd} vs [Q] (2 pages). Ordering information is given on any current masthead page.

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(17) It was confirmed that **1** is converted to rhodizonic acid (λ_{max} 360 nm) in the presence of $HClO_4$.[15]

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(20) Essentially the same results were obtained for methyl-*p*-benzoquinone (ΔH_f = −109, −77, and −127 kcal mol^{-1} for the **2**, **3**, and **4** type adducts, respectively) and chloro-*p*-benzoquinone (ΔH_f = −115, −86, and −134 kcal mol^{-1} for the **2**, **3**, and **4** type adducts, respectively).

(21) This mechanism is analogous to that suggested for the one-electron reduction of methylviologen.[8a]

(22) This may be the reason why the semiquinone radical anions derived from tetrasubstituted *p*-benzoquinone derivatives are not formed efficiently compared with those that have no site for the OH^- addition.[11] In the case of *p*-chloranil, nucleophilic substitution by OH^- is known to occur to yield chloranilic acid: Hancock, J. W.; Morrell, C. E.; Rhum, D. *Tetrahedron Lett.* **1962**, 987.

Specific, High-Efficiency, Triple-Helix-Mediated Cross-Linking to Duplex DNA

Jeng-Pyng Shaw, John F. Milligan, Steven H. Krawczyk,* and Mark Matteucci*

Gilead Sciences, Inc., 346 Lakeside Drive
Foster City, California 94404
Received December 12, 1990

The concept of sequence-specific cross-linking of nucleic acids was first suggested over two decades ago.[1] Since that time, numerous demonstrations have appeared.[2] Most of these involve the targeting of a single-stranded DNA or RNA with a deoxyoligonucleotide (DON) bearing a reactive moiety. The concept of sequence-specific double-stranded DNA recognition via triple-helix formation has recently been demonstrated,[3] and several examples of cross-linking to duplex DNA have been reported.[4] We report the high-efficiency cross-linking of DONs containing the modified nucleoside N_4,N_4-ethano-5-methyldeoxycytidine (**1**, Figure 1) to the N_7 of a specific guanine (G) in a double-stranded DNA target.

The deoxycytidine analogue **1** has previously been incorporated into DONs and been shown to specifically cross-link to single-stranded DNA.[5] Triple-helix formation via Hoogsteen base pairing occurs with the third strand binding in the major groove of the duplex.[3a] Substitution of the third-strand C of a C^+:G:C triplet with **1** would allow for the placement of the electrophilic methylene of **1** near the nucleophilic N_7 or O_6 sites of the G in the duplex (Figure 1).

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