to rotation in the parent amide are 18–20 kcal/mol (Table III). In imidate anions the greater double-bond character, as evidenced by the $^4J_{trans}$ of 1.5 Hz, ought to increase the barrier substantially. Therefore the mechanism for E/Z interconversion is not rotation, but nitrogen inversion. (Similar reasoning has been used previously to draw the same conclusion regarding imidate esters.[33])

Substituent and medium effects are as expected. The substituent effect at carbon has generally been considered to be small, on the basis of Hammett ρ values[34] and MO calculations.[35] Our results show that even the strong π donor, $-O^-$, does not change the inversion barrier substantially, relative to imines (e.g., $Me_2C{=}NPh$, $\Delta G^\ddagger$ = 20.3[36]) or imidate esters (e.g., MeC(O-*p*-tol)=NMe, $\Delta G^\ddagger$ = 20.2[33]). As for nitrogen substituents,[37] phenyl lowers the barrier to inversion because it can delocalize the 2p lone pair of the transition state. The bulky *tert*-butyl also lowers the barrier because interference with either formyl CH or $-O^-$ destabilizes the ground state.

With *N*-phenylformimidate anion it was also possible to demonstrate qualitatively a solvent effect on the inversion barrier. Although two stereoisomers were seen in protic solvents, only one set of NMR signals was seen in Me_2SO-d_6. This is not due to a predominance of a single stereoisomer (as in THF), since the kinetics of base-catalyzed exchange suggested that the two stereoisomers should be present in comparable amounts (Table II). Indeed, the chemical shifts observed in the aromatic region were consistent with a 3:1 mixture of *E* and *Z* forms, in rapid equilibrium. Apparently the barrier for *N*-phenylformimidate anion is so low in Me_2SO-d_6 that only an averaged spectrum is seen, but in protic solvents hydrogen bonding to the nitrogen lone pair retards the inversion so that the two forms can be seen.

(33) Satterthwait, A. C.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 7045.
(34) Hegarty, A. F.; Brady, K.; Mullane, M. *J. Chem. Soc., Perkin Trans. 2* **1980**, 535, and references cited.
(35) Leroy, G.; Nguyen, M.-T.; Sana, M.; Villaveces, J.-L. *Bull. Soc. Chim. Belg.* **1980**, *89*, 1023.
(36) Wurmb-Gerlich, D.; Vögtle, F.; Mannschreck, A.; Staab, H. A. *Justus Liebigs Ann. Chim.* **1967**, *708*, 36.
(37) Kalinowski, H.-O.; Kessler, H. *Top. Stereochem.* **1973**, *7*, 295. Lehn, J. M. *Fortschr. Chem. Forsch.* **1970**, *15*, 311.

Conclusions

We have demonstrated that soluble imidate anions, especially formimidate anions, $HCONR^-$, can be readily prepared by treating the amides with suitable bases. *N*-phenylformamide is a special case, since it is so acidic that its imidate anion can be prepared in hydroxylic solvents. The NMR spectra show that the *E* stereoisomer is usually more stable than the *Z*. We have thus verified the prediction made on the basis of the kinetics of base-catalyzed proton exchange, even though this is opposite to the stability order predicted by MO calculations. Solvent effects on the equilibrium suggest that the stability of the *E* stereoisomer is due to more favorable solvation or coulombic stabilization by the counterion. Unfortunately the data are not good enough to test the further quantitative prediction that the rates of exergonic proton transfer are independent of stereochemistry. The behavior of *N*-phenylformamide is unusual, since lyate-catalyzed proton exchange shows stereoselectivity, which is attributed to the operation of the Swain–Grunwald mechanism. The imidate anions could be reprotonated to produce the parent amides but in a nonequilibrium E/Z ratio characteristic of the anion; the equilibrium was then reestablished at a measurable rate. Imidate anions undergo nitrogen inversion, with barriers ca. 20 kcal/mol; substituent and solvent effects are as expected.

Acknowledgment. This research was supported by National Science Foundation Grants CHE78-12256 and CHE81-16800. C.-S.H. was a Fulbright Senior Researcher from Yonsei University, Seoul, Korea.

Registry No. 1 (R = R′ = Me), 77354-32-6; 1 (R = Et, R′ = Me), 95589-71-2; 1 (R = *t*-Bu, R′ = Me), 95589-72-3; 1 (R = Ph, R′ = Me), 87994-56-7; 1 (R = $PhCH_2$, R′ = Me), 95589-73-4; 1 (R = H, R′ = Me), 78715-78-3; 1 (R = H, R′ = *t*-Bu), 95589-74-5; 1 (R = H, R′ = $PhCH_2$), 95589-75-6; 1 (R = H, R′ = Ph), 55883-40-4.

Oxidation by Superoxide Ion of Catechols, Ascorbic Acid, Dihydrophenazine, and Reduced Flavins to Their Respective Anion Radicals. A Common Mechanism via a Sequential Proton–Hydrogen Atom Transfer

Donald T. Sawyer,* Thomas S. Calderwood, Carolyn L. Johlman, and Charles L. Wilkins*

Department of Chemistry, University of California, Riverside, California 92521

Received July 24, 1984

In aprotic media superoxide ion ($O_2^{-}\cdot$) reacts with 3,5-di-*tert*-butylcatechol ($DTBCH_2$), ascorbic acid, dihydrophenazine, and dihydrolumiflavin to produce their respective anion radicals. With $DTBCH_2$ in the gas phase an analogous oxidation by $O_2^{-}\cdot$ occurs. On the basis of this, the rapid pseudo-first-order kinetics for the reactions in the solution phase, and the efficient production of single products (the respective anion radicals), the primary process for the $O_2^{-}\cdot$–substrate reactions is concluded to be a sequential transfer of a proton and a hydrogen atom to give the anion radical. The anion radicals of phenazine and lumiflavin are rapidly oxidized by molecular oxygen. Hence, superoxide ion acts as an initiator for the autoxidation of dihydrophenazine and dihydrolumiflavin.

A recent study[1] has demonstrated that superoxide ion ($O_2^{-}\cdot$) oxidizes 1,2-diphenylhydrazine to the anion radical of azobenzene. The process is rapid ($k_{bi} > 100\ M^{-1}\ s^{-1}$) and, on the basis of kinetic studies and gas-phase ion–molecule

0022-3263/85/1950-1409$01.50/0

Table I. Products and Kinetics for the One-to-One Combination of 2 mM $(Me_4N)O_2$ and 2 mM Substrate in Dimethylformamide (0.1 M Tetraethylammonium Perchlorate) at 25 °C

substrate (S)[a]	anion radical/S[b]	H_2O_2/S exptl	H_2O_2/S calcd (eq 3b)	$k_1/[S]$,[c] M^{-1} s^{-1}
$DTBCH_2$	0.78 ± 0.20	0.90 ± 0.10	0.89	$(1.0 \pm 0.5) \times 10^4$ [d]
H_2Asc	0.80 ± 0.20	0.88 ± 0.10	0.90	$(1.8 \pm 0.5) \times 10^4$ [e]
H_2Phen	0.85 ± 0.20	0.98 ± 0.10	0.92	>560
H_2Fl	0.80 ± 0.20	0.91 ± 0.10	0.90	>340
PhNHNHPh	0.95 ± 0.10	0.98 ± 0.10	0.98	>100

[a] $DTBCH_2$, 3,5-di-*tert*-butylcatechol; H_2Asc, ascorbic acid, H_2Phen, dihydrophenazine, H_2Fl, dihydrolumiflavin. [b] The UV–visible absorption spectra for the anion radical products were compared with those for the products from controlled potential electrolytic reduction of 3,5-di-*tert*-butyl-*o*-benzoquinone (λ_{max} 340 and 380 nm),[11] dehydroascorbic acid (λ_{max} 360 nm),[12] phenazine,[4,13] lumiflavin (λ_{max} 420 nm),[4] and azobenzene (λ_{max} 410 nm).[1] [c] Pseudo-first-order rate constants, k_1 (normalized to unit substrate concentration [S]), were determined from current-collection-efficiency data ($O_2^{-}\cdot$ decay rates) with a glassy carbon–glassy carbon ring-disk electrode that was rotated at 900 rpm. ($O_2^{-}\cdot$ was produced at the disk electrode from dissolved O_2, which reacted with 2 mM substrate, and the unreacted $O_2^{-}\cdot$ was determined by its oxidation at the ring electrode.)[6,7] [d] $k_{bi} = 1 \times 10^4$ M^{-1} s^{-1} by stopped-flow spectrophotometry.[5] [e] $k_{bi} = 2.8 \times 10^4$ M^{-1} s^{-1} by stopped-flow spectrophotometry.[2]

measurements, appears to be a single step with the concerted transfer of an N–H proton and an N–H hydrogen atom (eq 1). In an earlier study[2] of the oxidation of

$$PhNHNHPh + O_2^{-}\cdot \rightarrow [PhNNPh]^{-}\cdot + H_2O_2 \quad (1)$$

ascorbic acid (H_2Asc) by superoxide ion a similar concerted proton–hydrogen atom transfer has been proposed (eq 2).

$$H_2Asc + O_2^{-}\cdot \rightarrow Asc^{-}\cdot + H_2O_2 \quad (2)$$

These results have prompted a renewed investigation of the oxidation by superoxide ion of catechols,[3] dihydrophenazine,[4] and dihydrolumiflavin[4] to ascertain if the primary process also involves a concerted proton–hydrogen atom transfer.

Although these earlier studies confirmed that acidic substrates such as catechol can induce the disproportionation of $O_2^{-}\cdot$ to H_2O_2 and O_2 via initial formation of $HO_2\cdot$,[5] the latter should be capable of removing a hydrogen atom from the catechol anion ($HCat^{-}$) to give the semiquinone anion radical ($SQ^{-}\cdot$). Likewise, the previous study[4] of dihydrophenazine and dihydrolumiflavin concluded that $O_2^{-}\cdot$ oxidized them to their fully oxidized forms, phenazine and lumiflavin. Although the initial results for the $O_2^{-}\cdot$–1,2-diphenylhydrazine investigation[1] indicated direct oxidation to azobenzene rather than to its anion radical ($[PhNNPh]^{-}\cdot$), subsequent measurements have established that dioxygen autoxidizes the latter to azobenzene. Hence, the earlier results for H_2Phen and H_2Fl probably were flawed by oxygen contamination.

Experimental Section

Equipment. Conventional electrochemical instrumentation, cells, and electrodes were employed for the cyclic voltammetric and controlled potential coulometric measurements.[5] A Pine Instruments Co. Model RDE 3 dual potentiostat, Model PIR rotator, and glassy carbon ring-disk electrode were used to make the kinetic measurements.[6] A Vacuum Atmosphere Corp. inert-atmosphere glovebox was used for the storage and preparation of solutions of tetramethylammonium superoxide.

Carey Model 17D and Model 219 spectrophotometers were used for the UV–visible spectrophotometric measurements. A Nicolet Analytical Instruments FTMS-1000 Fourier transform mass spectrometer with a 3.0 T superconducting magnet and a 2.54 cm × 2.54 cm × 7.62 cm trapped-ion cell was used for the study of gas-phase ion–molecule reactions.

Chemicals and Reagents. Burdick and Jackson "distilled in glass" UV grade solvents were used as received for most of the experiments. When necessary, acetonitrile was further dried by passing it through a column of Woelm N Super I alumina. Tetraethylammonium perchlorate (TEAP) from G. Frederick Smith Chemical Co. was dried in vacuo and used as the supporting electrolyte (0.1 M TEAP) in the electrochemical experiments. Other reagents and substrates were analytical grade or highest purity available and were used without further purification.

Methods. Measurements of the rate of the reaction of superoxide ion with various substrates were made with a rotated glassy carbon ring–disk electrode. The pseudo-first-order rate constants (k_{obsd}) were determined by the method that is described in a recent study of $O_2^{-}\cdot/RCCl_3$ reactions[6] and is developed in detail by Albery and Hitchman.[7]

Solutions of $O_2^{-}\cdot$ were prepared either by controlled potential electrolysis of O_2 (1 atm) or by dissoltion of weighed amounts of tetramethylammonium superoxide $[(Me_4N)O_2]$[8] The product solution from the stoichiometric combination of $(Me_4N)O_2$ with a solution of substrate was analyzed for O_2 and electroactive products by cyclic voltammetry. Aliquots (10 or 20 mL) of product solutions were assayed for hydrogen peroxide by dilution with 60–80 mL of water that contained 3% KI and 0.1 M HNO_3 and titration with thiosulfate.[9]

The product from the one-to-one combination of substrate and $(Me_4N)O_2$ in MeCN was prepared in a glovebox prior to its characterization by UV–visible spectroscopy. The anion radicals of 3,5-di-*tert*-butyl-*o*-benzoquinone, dehydroascorbic acid, phenazine, and lumiflavin were produced in a glovebox by controlled potential coulometric reduction in dimethylformamide.

Superoxide ion for the gas-phase ion–molecule reactions was produced from O_2 ($P = 5.2 \times 10^{-7}$ torr) with a 100-ms beam of 5.5-eV electrons. Trapping-plate potentials were −1 to −2 V. The trapped electrons were ejected by the application of a 5.1-MHz rf excitation to one of the trap plates for 1 ms. All ions formed by electron impact (except $O_2^{-}\cdot$) were ejected from the cell. A variable delay was used to allow the $O_2^{-}\cdot$ ions to react with the neutral substrate molecules; the anionic products of the reaction were detected by Fourier transform mass spectrometry (FTMS).[10]

Hydroxide ion was produced from H_2O molecules (P, 2×10^{-7} torr) by a 100-ms beam of 5.5-eV electrons. The catechol substrates were introduced via a direct insertion probe to give sample pressures of $(0.5–1.0) \times 10^{-7}$ torr.

(1) Calderwood, T. S.; Johlman, C. L.; Roberts, J. L., Jr.; Wilkins, C. L.; Sawyer, D. T. *J. Am. Chem. Soc.* **1984**, *106*, 4683.
(2) Sawyer, D. T.; Chiericato, G., Jr.; Tsuchiya, T. *J. Am. Chem. Soc.* **1982**, *104*, 6273.
(3) Nanni, E. J., Jr.; Stallings, M. D.; Sawyer, D. T. *J. Am. Chem. Soc.* **1980**, *102*, 4481.
(4) Nanni, E. J., Jr.; Sawyer, D. T. *J. Am. Chem. Soc.* **1980**, *102*, 7591.
(5) Chin, D.-H.; Chiericato, G., Jr.; Nanni, E. J. Jr., Sawyer, D. T. *J. Am. Chem. Soc.* **1982**, *104*, 1296.
(6) Roberts, J. L., Jr.; Calderwood, T. S.; Sawyer, D. T. *J. Am. Cem. Soc.* **1983**, *105*, 7691. The experimental details and data reduction procedure for the application of the voltammetric ring–disk method to the measurement of O_2^{-}–substrate reaction rates are summarized.
(7) Albery, W. J.; Hitchman, M. L. "Ring-Disc Electrodes"; Clarendon Press: Oxford, 1971.
(8) Sawyer, D. T.; Calderwood, T. S.; Yamaguchi, K.; Angelis, C. T. *Inorg. Chem.* **1983**, *22*, 2577.
(9) Ledaal, T.; Bernatek; *Anal. Chim. Acta* **1963**, *28*, 322.
(10) Johlman, C. L.; White, R. L.; Wilkins, C. L. *Mass Spectrom. Rev.* **1983**, *2*, 389–415.

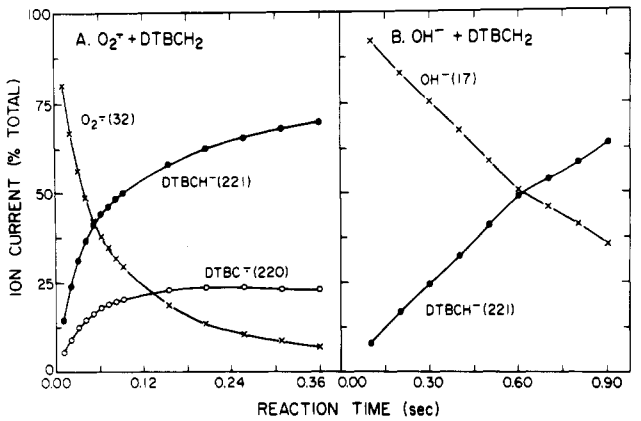


Figure 1. Time-resolved mass spectral intensities for the anions that result from the gas-phase reaction of 3,5-di-*tert*-butylcatechol (DTBCH$_2$; M_r = 222) with (A) $O_2^{-\cdot}$ and (B) OH^-.

Results

The product and the reaction kinetics for the 1:1 combination of $O_2^{-\cdot}$ [as $(Me_4N)O_2$] with 3,5-di-*tert*-butylcatechol, ascorbic acid, 1,2-diphenylhydrazine, dihydrophenazine, and dihydrolumiflavin in dimethylformamide (DMF) are summarized in Table I. For each substrate the dominant product is the anion radical species[1,4,11-13] that results from removal by $O_2^{-\cdot}$ of a proton and a hydrogen atom bound to a hetero atom. This process yields an essentially stoichiometric amount of H_2O_2 for each of the substrates in Table I.

The rates of reaction for $O_2^{-\cdot}$ with the individual substrates have been determined by the rotated ring-disk technique (O_2 is reduced at the disk to $O_2^{-\cdot}$, which reacts with substrate, and the unreacted $O_2^{-\cdot}$ is oxidized at the ring electrode),[6,7] and the normalized pseudo first-order rate constants are tabulated in Table I. Because the anion radical products from the $O_2^{-\cdot}$/substrate process for 1,2-diphenylhydrazine (PhNHNHPh), dihydrophenazine (H_2Phen), and dihydrolumiflavin (H_2Fl) react with the residual O_2 in the reaction cell to give $O_2^{-\cdot}$ (see below), the observed rate constants represent lower limits. In the case of 3,5-di-*tert*-butylcatechol and ascorbic acid, their anion radicals do not react with O_2.

Addition of dioxygen to the reaction vessel after the one-to-one combination of $O_2^{-\cdot}$ and PhNHNHPh, H_2Phen, or H_2Fl oxidizes the respective anion radicals to azobenzene, phenazine, and lumiflavin and yields a significant amount (20–50%) of $O_2^{-\cdot}$. The less than stoichiometric yield is probably due to trace water and H_2O_2 in the media, which induces the disproportionation of $O_2^{-\cdot}$.[14]

Addition of small quantities of $O_2^{-\cdot}$ [1 mM $(Me_4N)O_2$] in DMF to 10 mM H_2Phen in O_2-saturated DMF solution results in the complete oxidation of the substrate and the production of 9–10 mM H_2O_2. Most of the H_2Phen is converted to phenazine (~80%), but there are several decomposition products. The results for an analogus experiment with dihydroflavin are similar; 9–10 mM H_2O_2 and all of the substrate is oxidized. However, only a small fraction (<20%) of the H_2Fl is converted to lumiflavin.

Gas Phase Ion–Molecule Reactions. Figure 1A illustrates that $O_2^{-\cdot}$ reacts rapidly with 3,5-di-*tert*-butylcatechol (DTBCH$_2$) in the gas phase (P ~1 × 10^{-7} torr) to give its anion (DTBCH$^-$, m/z 221) and the anion radical of 3,5-di-*tert*-butyl-*o*-benzoquinone (DTBSQ$^{-\cdot}$, $\mu-/z$ 220) (in an approximate ratio of 3:1). Experiments with pyrocatechol [*o*-Ph(OH)$_2$] give similar results (approximate ratio 7:1), but with hydroquinone [*p*-Ph(OH)$_2$] the dominant product (~70%) is the anion radical (SQ$^{-\cdot}$, m/z 108). When the reagent is $^-$OH, the only product from the gas-phase reaction of DTBCH$_2$ (and of *o*-Ph(OH)$_2$) is its anion (Figure 1B). As expected, resorcinol [*m*-Ph(OH)$_2$] reacts with $O_2^{-\cdot}$ to yield a preponderance of its anion (m/z 109). Table II summarizes the gas-phase anion product distributions. These data show the trend which might be expected if radical anion stabilities govern product distribution.

Table II. Gas-Phase Product Distribution for Reaction of Superoxide Anion with Dihydroxybenzenes[a]

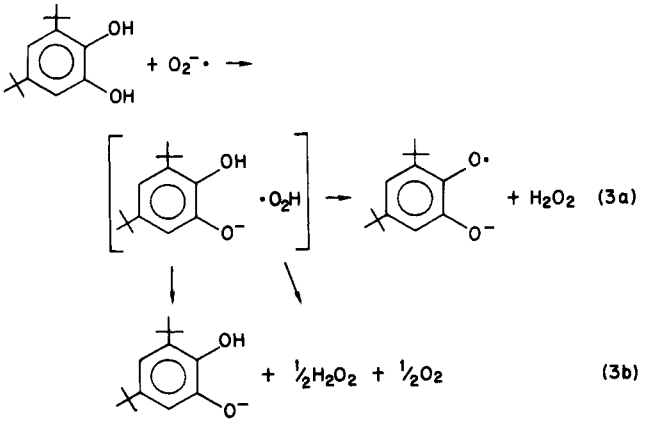
compound	M − 1[b]	M − 2	(M − 1)/(M − 2)
resorcinol[c]	82	4	20.5
catechol	77	10	7.70
hydroquinone	38	57	0.67
3,5-di-*tert*-butylcatechol	59	23	2.57

[a] 300-ms reaction time. [b] M − 1 anion at m/z 109 for the first three compounds and m/z 221 for the last. M − 2 in each case is the relative abundance of the radical anion. Abundances are percentage of total ions, the balance are unreacted $O_2^{-\cdot}$ anions. [c] 100-ms reaction time.

Discussion and Conclusions

The results that are summarized in Table I and Figure 1 confirm that $O_2^{-\cdot}$ oxidizes 3,5-di-*tert*-butylcatechol, ascorbic acid, dihydrophenazine, dihydrolumiflavin, and 1,2-diphenylhyrazine to their respective anion radicals. The dynamics and reaction stoichiometries for DTBCH$_2$ and H_2Asc (eq 2) are essentially the same (an earlier measurement of the $O_2^{-\cdot}$/H_2Asc reaction in DMF by stopped-flow spectrophotometry gave a second-order rate constant, k_{bi}, of 2.8 × 10^4 M^{-1} s^{-1}).[2]

The facility of the $O_2^{-\cdot}$/DTBCH$_2$ reaction, the absence of byproducts of intermediates in both the condensed-phase and gas-phase experiments, and the stoichiometric coefficients for reactants and products are consistent with a primary process that involves either (a) the concerted transfer from DTBCH$_2$ to $O_2^{-\cdot}$ of a proton and a hydrogen atom or (b) an initial proton transfer to form $HO_2\cdot$, which then abstracts a hydrogen atom from the anion (DTBCH$^-$) (eq 3a) or disproportionates (eq 3b). The gas-phase data



(Figure 1A) indicate that the lifetime of the complex is such that a significant fraction (~3/4) of the DTBCH$^-$ anion escapes. However, the 60% yield of anion radical from the gas-phase $O_2^{-\cdot}$/hydroquinone reaction indicates that this activated complex has sufficient lifetime to favor the concerted process (eq 3a). The condensed-phase data

(11) Stallings, M. D.; Morrison, M. M.; Sawyer, D. T. *Inorg. Chem.* **1981**, *20*, 2655.
(12) Sawyer, D. T.; Chiericato, G., Jr.; Tsuchiya, T. *J. Am. Chem. Soc.* **1982**, *104*, 6273.
(13) Sawyer, D. T.; Komai, R. Y. *Anal. Chem.* **1972**, *44*, 715.
(14) Sawyer, D. T.; Valentine, J. S. *Acc. Chem. Res.* **1981**, *14*, 393.

of Table I are most consistent with the sequential process for each of the substrates (combination of eq 3a and 3b). If the mechanism were exclusively concerted, the yield of H_2O_2 per substrate should be 1.0. The calculated yields on the basis of a combination of eq 3a and 3b ($[H_2O_2] = [DTBSQ^-\cdot) + {}^1/_2[DTBCH^-]$) that are tabulated in Table I are impressively close to the experimental values. If only the pathway of eq 3b occurred the yields would have been $0.5H_2O_2$ per S. The substantial yields of anion radical in the condensed phase relative to those in the gas phase are in accord with the expectation that the solvent cage of the activated complex should extend its lifetime and favor the sequential process (eq 3a). Hence, the major reactions for $DTBCH_2$ and H_2Asc with $O_2^-\cdot$ in aprotic solutions are represented by eq 4 and 5, respectively.

$$DTBCH_2 + O_2^-\cdot \xrightarrow{k_{bi} = 1.0 \times 10^4\ M^{-1}\ s^{-1}} DTSBQ^-\cdot + H_2O_2 \quad (4)$$

$$H_2Asc + O_2^-\cdot \xrightarrow{k_{bi} = 1.8 \times 10^4\ M^{-1}s^{-1}} Asc^-\cdot + H_2O_2 \quad (5)$$

The major process for the reaction of $O_2^-\cdot$ with dihydrophenazine and dihydrolumiflavin must be analogous to that of PhNHNHPh[1] to give the anion radicals of phenazine (eq 6) and lumiflavin (eq 7). These anion radicals are oxidized by O_2 to give $O_2^-\cdot$ plus phenazine (eq 8) and lumifalvin (eq 9), respectively. Thus, the processes

$$H_2Phen + O_2^-\cdot \xrightarrow{k_{bi} > 560\ M^{-1}\ s^{-1}} Phen^-\cdot + H_2O_2 \quad (6)$$

$$H_2Fl + O_2^-\cdot \xrightarrow{k_{bi} > 340\ M^{-1}\ s^{-1}} Fl^-\cdot + H_2O_2 \quad (7)$$

$$Phen^-\cdot + O_2 \rightarrow Phen + O_2^-\cdot \quad (8)$$

$$Fl^-\cdot + O_2 \rightarrow Fl + O_2^-\cdot \quad (9)$$

are equivalent to that for the anion radical of azobenzene ($[PhNNPh]^-\cdot$).[1] Because the oxidation potentials ($E_{p,a}$) for $Phen^-\cdot$[13] and 3-MeF.$^-$[15] in Me_2SO are −1.1 V vs. SCE and −0.8 V, respectively, reactions 5 and 6 are thermodynamically favored processes (the redox potential for the $O_2/O_2^-\cdot$ couple is −0.75 V).[14] Combination of eq 6 and eq 8 (and of eq 7 and eq 9) gives the overall stoichiometric process for the autoxidation of dihydrophenazine (eq 10) (and of dihydrolumifalvin (eq 11)). Turnover numbers of approximately ten are observed (with respect to production of H_2O_2) when catalytic quantities of $O_2^-\cdot$ are added to O_2-saturated solutions of H_2Phen or H_2Fl in DMF. Such an autoxidation of dihydroflumiflavin may be relevant to the fractional yield of $O_2^-\cdot$ from the flavin-mediated activation of O_2[16] and the autoxidation of xanthine (catalyzed by xanthine oxidase, a flavoprotein).[17]

$$H_2Phen + O_2 \xrightarrow{O_2^-\cdot} Phen + H_2O_2 \quad (10)$$

$$H_2Fl + O_2 \xrightarrow{O_2^-\cdot} Fl + H_2O_2 \quad (11)$$

The kinetic data of Table I confirm that each of the substrates rapidly converts superoxide to H_2O_2, apparently without formation of free perhydroxyl radical ($HO_2\cdot$). Although the radical anions that result from H_2Phen (eq 6) and H_2Fl (eq 7) are destroyed by dioxygen, those from catechol and ascorbic acid are stable in the absence of protons.

Acknowledgment. This work was supported by the National Science Foundation under Grants No. CHE-8212299 and CHE-8208073. Purchase of the FTMS-1000 mass spectrometer was supported under National Science Foundation Departmental Research Instrument Grant No. CHE-8217610. We are grateful for the constructive suggestions of the reviewers, especially with respect to the mechanistic interpretations.

Registry No. $DTBCH_2$, 1020-31-1; H_2Asc, 50-81-7; H_2Phen, 613-32-1; H_2Fl, 23542-56-5; PhNHNHPh, 122-66-7; superoxide, 11062-77-4; resorcinol, 108-46-3; catechol, 120-80-9; hydroquinone, 123-31-9.

(15) Sawyer, D. T.; Komai, R. Y.; McCreery, R. L. *Experientia, Suppl.* **1971**, *18*, 563.

(16) Hemmerich, P.; Wessick, A. "Biochemical and Clinical Aspects of Oxygen"; Caughey, W. S., Ed.; Academic Press: New York, 1979; pp 491–512.

(17) McCord, J. M.; Fridovich, I. *J. Biol. Chem.* **1968**, *243*, 5753.