Redox Mechanisms in an Ionic Matrix. Autocatalysis in the Process Superoxide + Nitrite $\rightleftharpoons$ Peroxide + Nitrate in Fused Salts

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Abstract: The kinetics of the process $2NO_2^- + 2O_2^- = 2NO_3^- + O_2^{2-}$ has been studied in fused alkali nitrates at 505°K, by detecting amperometrically the disappearance of superoxide as a function of time. The experimental curves obtained, representing the first known example of a continuously recorded kinetic process in molten salts, have been interpreted on the basis of the following autocatalytic mechanism: $NO_2^- + O_2^{2-} \rightleftharpoons NO_3^- + O^{2-}$ (a, forward; −a, reverse), $O^{2-} + O_2^- \rightarrow O_2^{2-} + O^-$ (b), $^1/_2(O^- + O^- \rightarrow O_2^{2-})$ (c). Working in excess nitrite, (a) represents the only rate-determining step at the beginning of the reaction, (b) becomes competitive with it after a certain reaction per cent, and (c) summarizes fast steps following the production of O^- free radicals. In the absence of an initial concentration of product, the autocatalytic process can be initiated by the slower, "direct" reaction between nitrite and superoxide (O_2^-) which produces peroxide (O_2^{2-}) in accordance with the reported overall process. On the basis of the proposed mechanism and the estimated rate constants, kinetic curves in good agreement with the experimental ones could be computed.

The anionic dimeric oxygen species peroxide (O_2^{2-}) and superoxide (O_2^-), often postulated[1-3] as labile intermediates in various redox reactions, are reasonably stable in several[4-10] ionic solvents, where they play[4-8] roles of primary importance. Recently, voltammetric studies performed in molten $(Na,K)NO_3$ eutectic as solvent have shown[5] the existence and the chemical reversibility of the reaction nitrite + superoxide = nitrate + peroxide. It is characterized by the following stoichiometry

$$2NO_2^- + 2O_2^- \underset{r}{\overset{f}{\rightleftharpoons}} 2NO_3^- + O_2^{2-} \qquad (1)$$

and its equilibrium quotient at 502°K is represented by the relation

$$[O_2^{2-}][NO_3^-]^2/[NO_2^-]^2[O_2^-]^2 = K_1 = 1.5 \times 10^{10}\ \text{mol}^{-1}\ \text{kg} \qquad (2)$$

Mechanistic information on this homogeneous system has so far been lacking and can be expected to contribute to a better understanding of the chemical behavior of peroxide and superoxide. For this reason a kinetic study of reaction 1 was performed. The experimental results obtained in the course of this study and the relevant mechanism derived from the results are presented and discussed in the present paper.

Experimental Section

Chemicals. An equimolar mixture of reagent grade molten sodium and potassium nitrate containing 0.5×10^{-3}–$0.5\ m$ nitrite was used as solvent. The potassium superoxide used contained not more than 2% potassium hydroxide. All experiments were performed under an atmosphere of nitrogen purified by contact with Ascarite (for CO_2), copper wool at 500° (for O_2), Drierite, magnesium perchlorate, and molecular sieves, at −80° (for moisture).

Apparatus and Procedures. The work was performed using the platinum-lined electrolysis cell previously[11] described. The indicator device was a platinum rotating disk electrode (rde) of 1.7×10^{-2} cm² in area. The aluminum block thermostat employed for the cell held a rotating magnet suitable for stirring the solution. A "three electrode" system was used to collect voltammetric and amperometric data. In this way the potential of the rde *vs.* the reference electrode ($Ag|Ag^+$ 0.07 *m*) was potentiometrically detected. At the same time currents were measured in a circuit consisting of the same rde and of a large-area "counter electrode."

Process 1 was studied from left to right and initiated by introducing small crystals of potassium superoxide in the melt containing a certain excess of nitrite. This procedure was possible because the high solubility[12] of superoxide permitted fast dissolution of KO_2 (5-10 sec under stirring conditions).

The kinetic data reported are relevant to the decrease of $[O_2^-]$ or to the increase of $[O_2^{2-}]$ as a function of time. Superoxide and peroxide, interrelated by the electrochemical equation

$$O_2^- + e = O_2^{2-} \qquad (3)$$

present in molten nitrates a well-defined polarographic wave, whose cathodic and anodic limiting currents have been found[4-6] to be proportional to $[O_2^-]$ and $[O_2^{2-}]$, respectively. This polarographic behavior made possible the experiment reported in Figure 1. However, in the course of the present work it was found that whenever the ratio $[O_2^-]/[O_2^{2-}]$ becomes very small, the anodic limiting current is, surprisingly, no longer proportional to $[O_2^{2-}]$. Because of this effect, when working at high nitrite concentrations, only superoxide could be precisely determined at any moment in the course of the reaction. The cathodic current, proportional to $[O_2^-]$, was recorded at constant potential ($\simeq -1.5$ V *vs.* the mentioned reference electrode) and continuous curves, such as those reported in Figures 2-4, were obtained. Temperature was maintained at 505 ± 0.5°K, *i.e.*, close to the melting point of the solvent used. The choice of this temperature was predicated[5] by a better resolution of the limiting current of superoxide.

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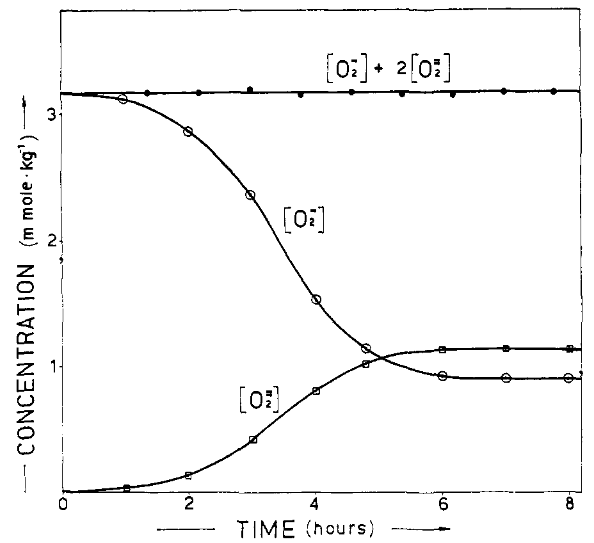

Figure 1. Kinetic curves relevant to the disappearance of O_2^- and production of O_2^{2-} in a melt originally containing 5.7×10^{-3} *m* nitrite and 3.16×10^{-3} *m* superoxide.

It was practically impossible to obtain significant kinetic information by following reaction 1 from the right to the left because of the rather low solubility (3-4 10^{-3} *m*) of O_2^{2-}. Thus the solubility process became the slow, rate-determining step of the reaction.

Results and Discussion

Data relevant to a preliminary study are reported in Figure 1. They represent the time-dependent variations of the peroxide and superoxide concentrations whenever reaction occurs in the presence of comparable concentrations of nitrite and superoxide. Superoxide concentrations decrease and peroxide concentrations increase until the equilibrium conditions represented by eq 2 are reached. At any time during the reaction it has been verified that

$$[O_2^-] + 2[O_2^{2-}] = \text{constant} \qquad (4)$$

as required by the stoichiometry of process 1. The most interesting information, from a mechanistic point of view, is certainly the S shape of the curves, typical[3] of an autocatalytic reaction. Quantitative data were obtained working in the presence of a large excess of nitrite ion so that most of the superoxide added could be reduced to peroxide. This permitted one to follow the kinetics of the forward process practically in absence of the back reaction. Representative examples of these experiments performed in the molal concentration ranges $0.12 < [NO_2^-] < 0.5$ and $1.5 \times 10^{-3} < [O_2] < 6 \times 10^{-3}$ are reported in Figures 2 and 3. Figure 2 represents kinetic curves recorded at the same concentration of nitrite, changing that of superoxide. Figure 3 reports examples of curves recorded at approximately the same initial concentration of superoxide, changing that of nitrite. These results show that the "time of reaction" is practically not influenced by the superoxide concentration (Figure 2), while, on the contrary, it is markedly dependent on that of nitrite (Figure 3). All the curves reported in Figures 1-3 were recorded in the absence of peroxide at the beginning of the reaction. Experiments performed in the presence of a certain initial concentration of O_2^{2-} (see Figure 4) have shown that, *ceteris paribus*, the induction phenomenon was less pronounced the higher the ratio $[O_2^{2-}]_0/[O_2^-]_0$, where $[O_2^{2-}]_0$ and $[O_2^-]_0$ indicate the concentrations of peroxide and superoxide present at the beginning of the experiment.

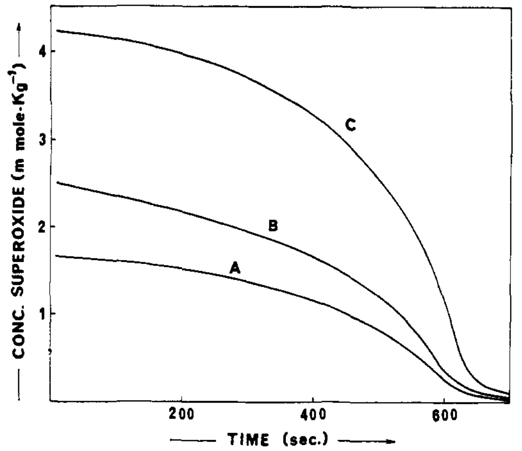

Figure 2. Kinetic profiles relevant to the disappearance of various initial concentrations of superoxide in a melt containing 0.5 *m* nitrite: A, $[O_2^-]_0 = 1.7 \times 10^{-3}$ *m;* B, $[O_2^-]_0 = 2.5 \times 10^{-3}$ *m;* C, $[O_2^-]_0 = 4.2 \times 10^{-3}$ *m.*

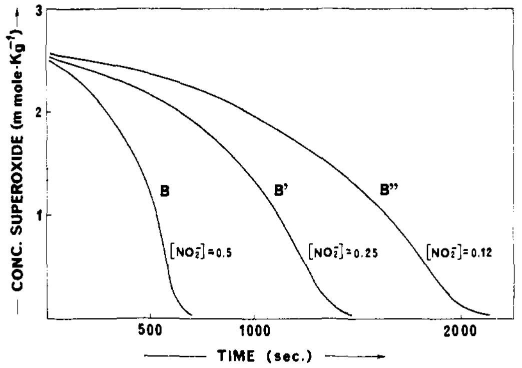

Figure 3. Kinetic profiles relevant to the disappearance of approximately the same superoxide concentration in a melt containing various concentrations of nitrite: B, $[NO_2^-] = 0.5$ *m;* B′, $[NO_2^-] = 0.25$ *m;* B′′, $[NO_2^-] = 0.12$ *m.*

Treatment of Data and Proposed Mechanism. The autocatalytic nature of process 1, which becomes apparent from an examination of the reported experimental curves, has been fully substantiated by plotting the reaction rate, $-\partial[O_2^-]/\partial t$, *vs.* the concentration of peroxide produced. The boldface curve in Figure 5 is a representative example of such diagrams. It is derived from the kinetic curve B in Figure 3 by reading the graphical slope at different times, $[O_2^{2-}]$ being calculated on the basis of eq 1 knowing the concentration of the superoxide which reacted. It is apparent that the initial portion of the curve can be represented by a straight line characterized by a positive intercept and a positive slope.

By considering the intercepts obtained in experiments performed at initial zero peroxide concentration, the relation

$$\left(-\frac{\partial[O_2^-]}{\partial t}\right)_{[O_2^{2-}]=0}\frac{1}{[NO_2^-][O_2^-]_0} = k_i = 5 \pm 1 \times 10^{-4}\ \text{mol}^{-1}\ \text{kg sec}^{-1} \qquad (5)$$

was verified, where $[O_2^-]_0$ is the initial concentration of superoxide. This finding seems to indicate the con-

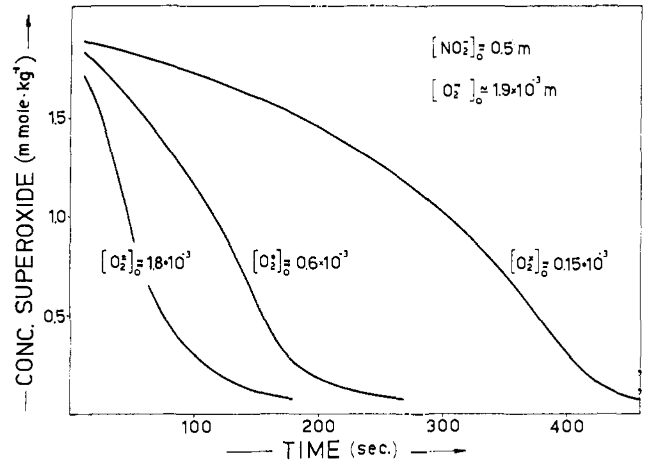

Figure 4. Disappearance of 1.9×10^{-3} *m* superoxide in a melt containing 0.5 *m* nitrite and the specified initial concentration of peroxide.

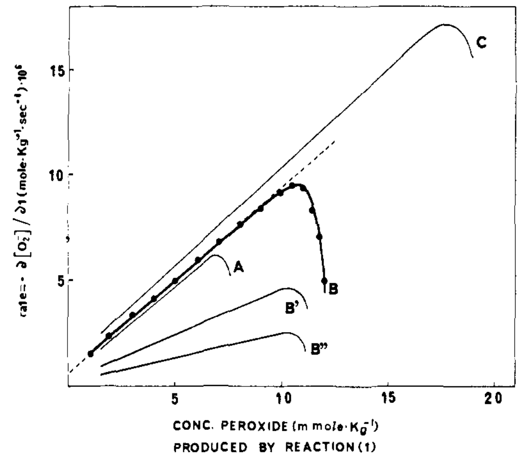

Figure 5. Comparison of rate *vs.* [O_2^{2-}] diagrams relevant to the curves, A, B, C, B′, and B′′, reported in Figures 3 and 4.

comitance of a slow uncatalyzed reaction between nitrite and superoxide, for instance, according to the process

$$NO_2^- + O_2^- \xrightarrow{i} NO_3^- + O^- \tag{6}$$

$$\tfrac{1}{2}(O^- + O^- \xrightarrow{\text{fast}} O_2^{2-}) \tag{7}$$

which is in agreement with the experimental relation 5 and the stoichiometry of reaction 1.

The dependence of the slope on the concentration of the various reacting species can be derived, for instance, by comparing the series of curves reported in Figure 5. The slope of the straight portions is practically independent of the initial superoxide concentration, while it depends on the concentration of nitrite. Within the specified superoxide and nitrite concentration ranges the relation

$$-\frac{\partial[O_2^-]}{\partial t}\frac{1}{[O_2^{2-}][NO_2^-]} = \text{constant} = 1.8 \pm 0.1 \times 10^{-2}\ \text{mol}^{-1}\ \text{kg sec}^{-1} \tag{8}$$

was verified.

On the basis of this relation, the simplest way of expressing the autocatalytic nature of reaction 1 is by the scheme

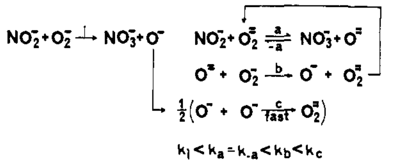

Figure 6. Proposed mechanism for the autocatalytic reduction of O_2^- by NO_2^- in molten (Na,K)NO_3 eutectic at 505°K.

$$NO_2^- + O_2^{2-} \underset{-a}{\overset{a}{\rightleftharpoons}} NO_3^- + O^{2-} \tag{9}$$

$$O^{2-} + O_2^- \xrightarrow{b} O_2^{2-} + O^- \tag{10}$$

$$\tfrac{1}{2}(O^- + O^- \xrightarrow{c} O_2^{2-}) \tag{7}$$

The forward process, a, of reaction 9 represents the rate-determining step during the first part of the reaction, where the plot $-\partial[O_2^-]/\partial t$ *vs.* [O_2^{2-}] is a straight line. It should be pointed out that the existence, under the present experimental conditions, of the first step of the proposed mechanism, has been previously[4-6] stated. The estimated[5] equilibrium constant is

$$[NO_2^-][O_2^{2-}]/[NO_3^-][O^{2-}] = K_9 = \frac{k_{-a}}{k_a} = 3 \tag{11}$$

As long as (a) remains the rate-determining step of the autocatalytic process, the reaction rate can be written (see relations 5, 8, and 9)

$$\text{rate} = -\frac{\partial[O_2^-]}{\partial t} = k_a[NO_2^-][O_2^{2-}] + k_i[NO_2^-][O_2^-] \tag{12a}$$

and by introducing $[O_2^-]_0$, the value of the superoxide concentration at the beginning of the reaction, it follows that

$$\text{rate} = -\frac{\partial[O_2^-]}{\partial t} = (k_a - 2k_i)[NO_2^-][O_2^{2-}] + k_i[NO_2^-][O_2^-]_0 \tag{12b}$$

which represents (the nitrite concentration is a constant under the present experimental conditions) the equation of the experimental straight lines. By comparing expressions 5, 8, and 12a, one derives

$$k_a = 1.7 \pm 0.1 \times 10^{-2}\ \text{mol}^{-1}\ \text{kg sec}^{-1} \tag{13}$$

and then, on the basis of relation 11, an approximate value of k_{-a}. The deviation from linearity of the derivative curves in Figure 5 indicates that (at least) one other determining step becomes competitive with (a) after a certain reaction period. The rates of the two processes will be comparable in the region of the maximum, while (see Figure 5) the influence of (a) rapidly decreases in the last per cents of reaction.

A confirmation of the proposed autocatalytic mechanism, summarized for convenience in Figure 6, can be obtained by a mathematical analysis of the reacting system.

Stationary-State Technique. It was *a priori* supposed that process b is the step which becomes competitive with (a) in the course of the reaction. On the basis of this hypothesis, by applying (see Appendix) the steady-state condition to the reaction intermediate, O^{2-}, the rate of the process can be expressed

$$\text{rate} = -\frac{\partial[O_2^-]}{\partial t} = \frac{k_a k_b[NO_2^-][O_2^-][O_2^{2-}]}{k_{-a}[NO_3^-] + k_b[O_2^-]} + k_i[NO_2^-][O_2^-] \quad (14)$$

By differentiating eq 14 with respect to $[O_2^{2-}]$ and setting the result equal to zero, the "maximum condition" for the derivative curves exemplified in Figure 5 can be written

$$[O_2^{2-}]_M = \frac{\bar{B}\bar{A} \pm \sqrt{\bar{B}\bar{A}(\bar{B}\bar{A} - \bar{C})}}{2\bar{A}} \quad (15)$$

where

$$\bar{A} = (k_a k_b - 2k_i k_b)$$

$$\bar{B} = [O_2^-]_0 + (k_{-a}/k_b)[NO_3^-]$$

$$\bar{C} = k_a k_b[O_2^-]_0 - 2k_i k_b\{[O_2^-]_0 + (k_{-a}/k_b)[NO_3^-]\}$$

and $[O_2^{2-}]_M$ is the concentration of peroxide corresponding to the maximum.

In accordance with the experimental findings (see curves B, B′, and B″ in Figure 4) relation 15 indicates that the position of the maximum is independent of the nitrite concentration. By substituting in eq 15 the known values of $[O_2^-]_0$, the corresponding experimental values of $[O_2^{2-}]_M$, and the constants k_i, k_a, and k_{-a} derived from relations 5, 11, and 13 one obtains

$$k_b = 4 \pm 1 \times 10^3 \text{ mol}^{-1} \text{ kg sec}^{-1} \quad (16)$$

The numerical value represents the average of data obtained from experiments performed in the specified superoxide and nitrite concentration ranges. The low precision is probably due to the practical difficulty of determining the correct position of the maximum. The most reliable of the two k_b values obtained from eq 15 was selected by using a "best-fitting" method based on eq 17 (*vide infra*).

It should be noted that, at zero peroxide concentration, relation 14 becomes equal to eq 5. Furthermore, as long as $k_{-a}[NO_3^-]$ remains negligible compared to $k_b[O_2^-]$, eq 14 can be reduced to relation 12a. As seen, this relation explains the linear shape of the first part of the curves reported in Figure 5. These curves will begin to deviate from the initial linearity when the values of the two above-mentioned terms tend to become comparable ($k_{-a}[NO_3^-]$ is a constant and $k_b[O_2^-]$ gets smaller and smaller in the course of the reaction).

Simulated Kinetics. By integrating eq 14, one obtains

$$t = (\alpha - \delta) \ln \frac{\beta + \gamma[O_2^-]}{\beta + \gamma[O_2^-]_0} - \alpha \ln \frac{[O_2^-]}{[O_2^-]_0} \quad (17)$$

where the constants α, β, γ, and δ have the values reported in the Appendix.

Equation 17 was used to simulate a chemical process characterized by the proposed mechanism and by the reported rate constants. The computed kinetic curves fitted the corresponding experimental ones well, up to 94–96% of reaction after which they tended toward higher slopes. This discrepancy can be indicative of a certain influence on the reaction rate of processes, such as those involving O^- free radicals, or the disproportionation of superoxide, which were neglected in the course of the mathematical formulation. However, this could not be stated conclusively, either because of the limitations of the analytical technique at low concentrations or because the discrepancy was partly due to the back-reaction, since the kinetic processes were incomplete to the extent of about 1%.

Reproducibility and Consistency of Results. The reproducibility and consistency of the results reported in the present communication were critically contingent on the use of a perfectly dry melt. Small concentrations of water, obtained, for example, by flowing commercial UPP nitrogen (used without further purification), were sufficient to produce an appreciable slowing of the rate. By considering the reaction scheme reported in Figure 6, this phenomenon seems due to the process

$$O^{2-} + H_2O = 2OH^- \quad (18)$$

It can occur, either by the direct reaction between O^{2-} and water, or by the alternate indirect path according to

$$\begin{array}{cr} O_2^{2-} + H_2O = 2OH^- + {}^1/_2O_2 & (19) \\ {}^1/_2O_2 + O^{2-} = O_2^{2-} & (20) \\ \hline O^{2-} + H_2O = 2OH^- & (18) \end{array}$$

The estimated[5] equilibrium constant for reaction 20 is, in fact, quite high

$$[O_2^{2-}]^2/[O_2][O^{2-}]^2 = K_{20} = 3 \times 10^{16} \text{ mol}^{-1} \text{ kg} \quad (21)$$

and it is known[9] that O^{2-} can easily react with molecular oxygen in ionic solvents.

A preferential reaction of water with O_2^- according to

$$2O_2^- + H_2O = 2OH^- + {}^3/_2O_2 \quad (22)$$

seems to be excluded. In this case, one would expect the disappearance of superoxide either to be accelerated or, perhaps, to remain uninfluenced but not to be inhibited by the presence of moisture, as found experimentally.

Another process which could influence the reaction mechanism is the disproportionation[5] of superoxide

$$2O_2^- = O_2 + O_2^{2-} \quad (23)$$

$$[O_2^{2-}][O_2]/[O_2^-]^2 = K_{23} = 3 \times 10^{-6}$$

However, recent[4–10] findings seem to indicate that superoxide, in ionic solvents, is stable for quite long periods, even under flux of an inert gas or under vacuum which can favor the elimination of oxygen. It cannot be excluded, however, that some peroxide can be produced according to eq 23, especially when solid KO_2 is introduced in the melt. Reaction 23 (which is, likely, a second-order process) can, in fact, be favored by the very high concentrations of O_2^- present before the complete dissolution of KO_2. From this point of view k_i in relation 5 should be considered the maximum (rather than the absolute) value of the kinetic constant for process 6. An initial concentration of O_2^{2-} would, in fact, contribute (according to process 9) to the intercept's value of the straight line in Figure 5, which was used to obtain relation 5.

As a final remark it might be interesting to note that the prevalence of an autocatalytic process for reaction 1 appears to be due to the higher reactivity of NO_2^- with O_2^{2-} ($k_a = 1.7 \times 10^{-2}$ mol^{-1} kg sec^{-1}) rather than with O_2^- ($k_i \leqslant 5 \times 10^{-4}$ mol^{-1} kg sec^{-1}), notwithstanding the stronger oxidizing nature of this last species. The oxygen–oxygen bond (stronger[13] in O_2^- than in O_2^{2-}) can have, in this case (as often in redox processes) a certain influence on the reaction rates. This hypothesis seems in agreement with the extremely low rates observed, in preliminary experiments, for reactions between nitrite and molecular oxygen whose O–O bond is certainly stronger[13] than those of its negative ions O_2^- and O_2^{2-}. Further pertinent work to elucidate this question is in progress.

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Appendix

Derivation of Eq 14. By applying the stationary-state condition to the species O^{2-} involved in the autocatalytic mechanism presented in Figure 6

$$d[O^{2-}]/dt = k_a[NO_2^-][O_2^{2-}] - k_{-a}[NO_3^-][O^{2-}] - k_b[O^{2-}][O_2^-] = 0 \quad (I)$$

one obtains $[O_2^{2-}]$. The rate of disappearance of superoxide is

$$-d[O_2^-]/dt = k_b[O^{2-}][O_2^-] \quad (II)$$

Equation 14 can be derived from (II) by adding the term $k_i[NO_2^-][O_2^-]$ which expresses the contribution of the parallel "direct" reaction between NO_2^- and O_2^-.

Derivation of Eq 17. Equation 14 can be reduced (by substituting $[O_2^{2-}]$ with $([O_2^-]_0 - [O_2^-])/2$) to

$$-dt = \frac{B + Dx}{x[(Ax_0 + BC) + (CD - A)x]}\,dx \quad (III)$$

where $A = k_ak_b[NO_2^-]/2$, $B = k_{-a}[NO_3^-]$, $C = K_i \cdot [NO_2^-]$, $D = k_b$, $x_0 = [O_2^-]_0$, and $x = [O_2^-]$. Upon integration, the value of the integration constant can be calculated from the limiting condition $t = 0$. Equation 17 can be readily obtained by setting $\alpha = B/(Ax_0 + BC)$, $\beta = Ax_0 + BC$, $\gamma = CD - A$, and $\delta = D/(CD - A)$.

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Theoretical Studies of the Ground and Excited Electronic States of the Benzynes by *Ab Initio* Self-Consistent-Field and Configuration-Interaction Methods[1]

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Abstract: *Ab initio* self-consistent-field (SCF) and configuration-interaction (CI) calculations on *o*-, *m*-, and *p*-benzyne are reported for the molecules in a geometry constrained to be that of benzene. The results predict conclusively that the ground electronic state of *o*-benzyne is a singlet. The meta and para isomers are found to have triplet ground states in the geometries considered; however, the singlet–triplet energy separations are quite small. Electronic spectral calculations for *o*-benzyne show the existence of both $n \rightarrow n^*$ and $\pi \rightarrow \pi^*$ states near the region of the experimentally observed intense absorption; also a $\pi \rightarrow n^*$ transition is found at longer wavelength. An important conceptual aspect of the study is the failure of a single-determinant SCF wave function to describe adequately the weak additional bond between the dehydrocarbon atoms in the case of a singlet state. It is shown that for a proper description at least a two-determinant (CI) wave function is required both in principle and in practice.

Since the work of Roberts confirmed the intermediacy of the species *o*-benzyne (1,2-dehydrobenzene) in the amination of aryl halides by metal amides in liquid ammonia,[2] *o*-benzyne has been proposed as an intermediate in a number of reactions.[3] Generally, it is assumed that the ground state of *o*-benzyne is of singlet multiplicity, but no definitive proof of this assertion has as yet been given. In fact, the contrary assumption, that the ground state of *o*-benzyne is a triplet, has also been proposed.[4]

Several semiempirical calculations concerning the nature of the ground electronic state of *o*-benzyne have been reported recently.[5–8] Also, the correspond-

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