molecules, and each molecule (assuming C_2 local molecular symmetry) provides two measures of some of the molecular parameters. Figure 3 shows the mean values and the individual estimates of the bond lengths and angles along with estimates of the standard deviations as given by the least-squares variance–covariance matrix. These estimated standard deviations, although large, are clearly not large enough to reconcile some individual distances and angles with "reasonable" limiting values. No full interpretation can be offered here, but these unreasonable distances and angles may reflect substantial chemical decomposition resulting from exposure to the X-ray beam. Alternatively, the presence in the crystal of a certain fraction of *trans*-cyclooctene with the conformation as in Figure 1b, perhaps produced by radiation, is a possibility. The structure is not yet refined sufficiently to test these hypotheses satisfactorily. Notwithstanding the apparently consistent, large differences in the C_4–C_5, C_6–C_7 distances for the two molecules, we do not believe that a real deviation of the molecules from C_2 local symmetry should be conclusively inferred. The α-methylbenzylamine moieties appear to be normal in all respects within the uncertainties implied by the indicated standard deviations.

The angle of twist of the double bond—the 8,1,2,3 dihedral angle—we estimate as 43.5° (mean of 39.8° for A, 47.2° for B). The mean $C_1{=}C_2$ double bond distance of 1.35 Å is compatable with the value 1.354 Å obtained for ethylene in Zeise's salt, $KPtCl_3(C_2H_4)\cdot H_2O$, by Hamilton, Klanderman, and Spratley[7] in a neutron diffraction study. For the mean Pt–C distance for carbon atoms of the double bond we find 2.11 Å, also in agreement with that found in Zeise's salt, 2.14 Å. For the mean Cl–Pt–Cl angle, we obtain the value 175.4 ± 0.2°.

The conformation for (−)-*trans*-cyclooctene was determined in this study from a difference electron-density map phased on the platinum, chlorine, and α-methylbenzylamine atoms alone; the structure was not biased by any premature attempt to locate the (−)-*trans*-cyclooctene rings. The *R* absolute configuration reported here for the (−)-*trans*-cyclooctene was determined not only by reference to the known absolute configuration of the (+)-α-methylbenzylamine but also by consideration of the Bijovet differences $F_{hkl} - F_{\bar{h}\bar{k}\bar{l}}$. Our findings concerning the absolute configuration are in accord with the conclusions of Cope and are thus contrary to the prior predictions of Moscowitz and Mislow.

We hope to publish the completely refined structure at a later date. A table of intermediate atomic coordinates is available from the authors.

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Evidence for the Formation of Hydroxyl Radicals in the Isomerization of Pernitrous Acid to Nitric Acid in Aqueous Solution

Sir:

Pernitrous acid, HOONO, has been detected as a short-lived intermediate in the reaction of nitrite ion with hydrogen peroxide,[1–3] in the photolysis of aqueous solutions of nitrate ion at wavelengths shorter than 2800 Å,[4,5] and in the recently reported reaction of hydroxyl radicals with nitrogen dioxide in water.[6] Although there is ample evidence that pernitrous acid rapidly[6,7] and quantitatively[1–3] isomerizes to nitric acid, H–O–NO_2, the mechanism of the isomerization has not been elucidated. In the present report experimental evidence is presented which is consistent with the view that the isomerization of pernitrous acid to nitric acid in aqueous solutions in the temperature range of 15–35° proceeds by means of a homolytic decomposition of pernitrous acid to produce a 32% yield of chemically reactive hydroxyl radicals and nitrogen dioxide.

We have observed the reproducible evolution of oxygen from aqueous solutions, saturated with oxygen or nitrogen, containing sodium nitrite (0.005–0.08 *M*), hydrogen peroxide (greater than 1.0 *M*), EDTA (2.0 × 10^{-5} *M*),[8] and phosphate buffer (0.5 *M*) to maintain constant pH (4.8–5.2). The oxygen evolution was strongly retarded by the known hydroxyl radical scavengers, acetate and benzoate ions and isopropyl alcohol. The concentrations of these additives were sufficiently low (0.05 *M*) that no reaction of these species with nitrite ion, determined spectrophotometrically at 3450 Å, occurred in the absence of hydrogen peroxide. As a result of these observations a systematic study of the relationship between the observed rate of oxygen evolution and the rate of consumption of nitrite ion was carried out.

At a constant concentration of hydrogen peroxide the rate of disappearance of nitrite ion, $[-d(NO_2^-)/dt]_t$, determined spectrophotometrically in thermostated cells, was found to be first order in nitrite and second order in hydrogen ion at the three temperatures, 15, 25, and 35°, as reported in the earlier work at 25°.[3] The rate of oxygen evolution from the same solutions as a function of time, $[+d(O_2)/dt]_t$, was determined by means of the automatic recording gas apparatus utilized in earlier studies.[9] A typical plot of the ratio $[-d(NO_2^-)/dt]_t/[+dO_2/dt]_t$ *vs.* $(NO_2^-)_t/(H_2O_2)$ determined with two different initial nitrite concentrations is presented in Figure 1. At the three temperatures and two different hydrogen peroxide concentrations the results are accurately described by the expression

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[8] In the absence of EDTA, the rates obtained with triply distilled water were erratic and generally higher than those observed in the presence of EDTA. Addition of EDTA (0.5 × 10^{-5} to 5.0 × 10^{-5} *M*) resulted in a constant rate. The function of EDTA is to complex trace metal ions which engage in reactions with hydroperoxy free radicals leading to additional oxygen evolution; *vide infra.*

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$$\left[\frac{-\mathrm{d}(\mathrm{NO_2^-})}{\mathrm{d}t}\right]_t \Bigg/ \left[\frac{+\mathrm{d}(\mathrm{O_2})}{\mathrm{d}t}\right]_t = a + b(\mathrm{NO_2^-})_t/(\mathrm{H_2O_2}) \tag{A}$$

The values of *a* and *b* are summarized in Table I.

Table I. Summary of Values of Slopes and Intercepts from Plots of $[-\mathrm{d}(\mathrm{NO_2})/\mathrm{d}t]_t/[+\mathrm{d}(\mathrm{O_2})/\mathrm{d}t]_t$ *vs.* $(\mathrm{NO_2^-})_t/(\mathrm{H_2O_2})$ and Values of k_5/k_6 and *f* Calculated from (B)[a]

$[\mathrm{H_2O_2}]$, *M*	Temp, °C	*a*	*b*	k_5/k_6	*f*
1.13	15.0	5.7 ± 0.4	910 ± 60	136 ± 9	0.30 ± 0.02
	25.0	4.9 ± 0.5	660 ± 70	112 ± 12	0.34 ± 0.03
	35.0	5.6 ± 0.5	510 ± 40	77 ± 6	0.30 ± 0.03
1.87	15.0	4.8 ± 0.4	920 ± 80	158 ± 13	0.34 ± 0.03
	25.0	5.2 ± 0.4	560 ± 40	90 ± 6	0.32 ± 0.03
	35.0	5.2 ± 0.4	340 ± 30	55 ± 5	0.32 ± 0.03

[a] Uncertainties calculated from standard errors of estimate from least-squares treatment of the data.

A reaction scheme consistent with this expression is the following

$$\mathrm{H^+ + NO_2^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{HNO_2} \tag{1}$$

$$\mathrm{HNO_2 + H^+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{NO^+ + H_2O} \tag{2}$$

$$\mathrm{NO^+ + H_2O_2} \xrightarrow[k_3]{} \mathrm{HOONO + H^+} \quad \text{(slow)} \tag{3}$$

$$\mathrm{HOONO} \xrightarrow{fk_4} \mathrm{HO\cdot + NO_2} \tag{4}$$

$$\mathrm{HO\cdot + NO_2^-} \xrightarrow{k_5} \mathrm{HO^- + NO_2} \tag{5}$$

$$\mathrm{HO\cdot + H_2O_2} \xrightarrow{k_6} \mathrm{H_2O + HO_2\cdot} \tag{6}$$

$$\mathrm{2HO_2\cdot} \xrightarrow{k_7} \mathrm{H_2O_2 + O_2} \tag{7}$$

$$\mathrm{2NO_2 + H_2O} \xrightarrow{k_8} \mathrm{HNO_3 + HNO_2} \tag{8}$$

where *f* represents the fraction of pernitrous acid which yields hydroxyl radical and nitrogen dioxide. Utilizing a steady-state assumption for HO·, $\mathrm{HO_2\cdot}$, HOONO,[10] and $\mathrm{NO_2}$[11]

$$\frac{-\mathrm{d}(\mathrm{NO_2^-})}{\mathrm{d}t} = k_4(\mathrm{HOONO}) - {}^1/_2 fk_4(\mathrm{HOONO}) + {}^1/_2 k_5(\cdot\mathrm{OH})(\mathrm{NO_2^-})$$

$$\frac{+\mathrm{d}(\mathrm{O_2})}{\mathrm{d}t} = {}^1/_2 k_6(\cdot\mathrm{OH})(\mathrm{H_2O_2})$$

And since

$$(\cdot\mathrm{OH}) = \frac{fk_4(\mathrm{HOONO})}{k_5(\mathrm{NO_2^-}) + k_6(\mathrm{H_2O_2})}$$

we may write

$$\frac{-\mathrm{d}(\mathrm{NO_2^-})}{\mathrm{d}t} \Bigg/ \frac{+\mathrm{d}(\mathrm{O_2})}{\mathrm{d}t} = \left(\frac{2}{f} - 1\right) + \left(\frac{2}{f}\right)\frac{k_5}{k_6}\frac{(\mathrm{NO_2^-})}{(\mathrm{H_2O_2})} \tag{B}$$

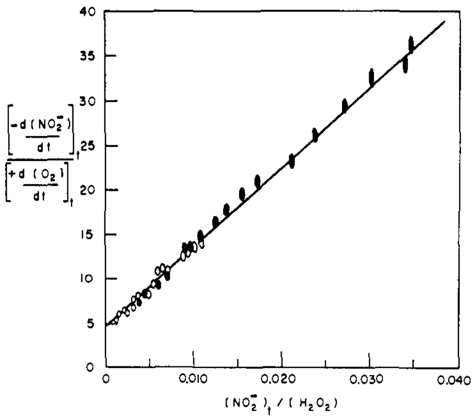

Figure 1. A plot of $[-\mathrm{d}(\mathrm{NO_2^-})/\mathrm{d}t]_t/[+\mathrm{d}(\mathrm{O_2})/\mathrm{d}t]_t$ *vs.* $(\mathrm{NO_2^-})_t/(\mathrm{H_2O_2})$ at 15° and pH 4.80 for solutions containing 1.87 *M* $\mathrm{H_2O_2}$, 2×10^{-5} *M* EDTA, and 0.5 *M* phosphate buffer, with initial concentrations of $\mathrm{NaNO_2}$ of (●) 0.72 and (○) 0.024 *M*.

The literature values obtained from pulse radiolysis experiments at or slightly above room temperature vary for k_5 from 2.5×10^9 to 3.5×10^9 M^{-1} sec^{-1} and for k_6 from 1.2×10^7 to 4.0×10^7 M^{-1} sec^{-1}.[12] The values of the ratio k_5/k_6 calculated from eq B and our experimental results (Table I) are therefore consistent with those calculated from the literature values. Moreover, the temperature coefficient for the experimental ratio varies in a manner which would be anticipated for a hydrogen atom transfer from a solvated O-H bond, reaction 6, compared to a diffusion-controlled electron transfer, reaction 5.

Further support for the homolytic decomposition of pernitrous acid is obtained from the following analysis. Consider the cycle

$$\begin{tikzcd}
\mathrm{HO{-}NO_2(aq)} \arrow[d, "\Delta H_1"] & \mathrm{HO\cdot(aq) + NO_2(aq)} \arrow[l, "\Delta H_4"'] \\
\mathrm{H^+(aq) + O^-{-}ONO(aq)} \arrow[r, "\Delta H_2"] & \mathrm{HOONO(aq)} \arrow[u, "\Delta H_3"']
\end{tikzcd}$$

On the assumption that ΔH_4 in aqueous solution is equal to the gas-phase value, −49.0 kcal/mol, and utilizing the reported value of ΔH_1, +38.8 ± 2.0 kcal/mol,[13] a value of $\Delta H_2 + \Delta H_3 = 10.0 \pm 2.0$ kcal/mol is calculated. This value compares favorably with the value of 12.5 kcal/mol[14] reported for the activation energy for the isomerization of pernitrite anion to nitrate anion, which proceeds *via* pernitrous acid[6,7,14] and therefore corresponds to $\Delta H_2 + \Delta E_3^{\ddagger}$.

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(10) The half-life of pernitrous acid is extremely short[5–7] compared with the duration of the experiments.

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The Synthesis of a Stable 8-π-Electron Thiepin

Sir:

The electronic description of heterocyclic systems which do not satisfy the Hückel rule has long been a