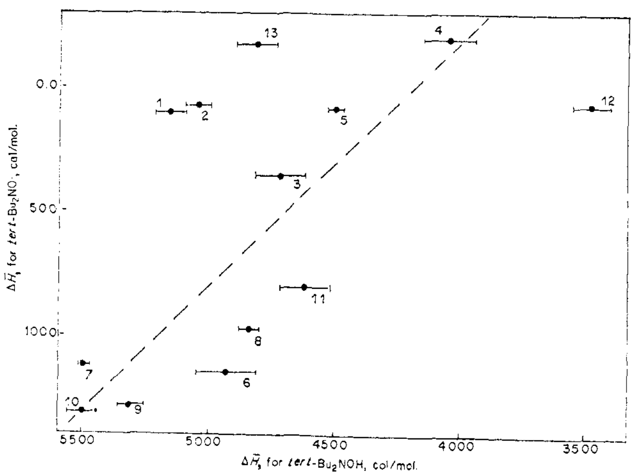
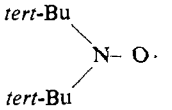


Figure 1. Solution heats at infinite dilution for **1** and **2**. Solvents: 1, benzene; 2, toluene; 3, nitrobenzene; 4, benzonitrile; 5, anisole; 6, *n*-hexane; 7, *n*-heptane; 8, isooctane; 9, decalin; 10, cyclohexane; 11, cyclohexene; 12, *tert*-$C_5H_{11}OH$; 13, CCl_4.

analog di-*tert*-butylhydroxylamine (**2**) in 13 solvents. The results are interpreted in a way which lends direct thermodynamic support to the idea that aromatics are more effective solvents than alkanes for free radicals.



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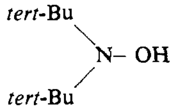

2

The heat of solution at infinite dilution for a given solute may be analyzed as a composite of enthalpy terms.[3] These are vaporization of the solute (ΔH_{vap} or ΔH_{sub}, endothermic), formation of solute-sized cavities in the solvent (ΔH_{cav}, endothermic), and interaction of solute with solvent or solvation (ΔH_{solv}, exothermic). The variation in $\Delta \bar{H}_s$ for a single solute in a series of organic solvents is expressed by

$$\delta_M \Delta \bar{H}_s = \delta_M \Delta H_{\text{solv}} + \delta_M \Delta H_{\text{cav}}$$

since vaporization heat will be a constant. Clearly $\delta_M \Delta \bar{H}_s$ does not show variations in solvating ability alone, but reflects both solvation and cavity heat variations. However, if the size and shape of two solutes are essentially the same, as for **1** and **2**, then differences in $\delta_M \Delta \bar{H}_s$ for the two in the same series of solvents will accurately reflect differences in changes in solvation for the two species.

In Figure 1 are plotted $\Delta \bar{H}_s$ values for the nitroxide *vs.* those for the hydroxylamine. If cyclohexane is taken as a reference solvent, then the dashed 45° line represents the locus of potential points for transfer of **1** and **2** from cyclohexane to another solvent by a process in which $\delta_M \Delta H_{\text{cav}}$ and $\delta_M \Delta H_{\text{solv}}$ are the same for both solutes. Since $\delta_M \Delta H_{\text{cav}}$ is assumed to be essentially the same for **1** and **2**, all points would appear on this line if it were not for differences in solvation enthalpy change (solvation enthalpy of transfer). A deviation of a point from the line in the *X* or *Y* direction is thus a direct measure of difference in solvation enthalpy of transfer for the two solutes from cyclohexane to a given solvent.

It is clear that in transfer from cyclohexane to all but one of the alkanes and to *tert*-amyl alcohol the hydroxylamine undergoes a more favorable enthalpy of solvation change than does the free radical. For transfer to cyclohexene, *e.g.*, the hydroxylamine is favored by 3–500 cal/mol. In contrast, on transfer to any of the aromatics and CCl_4 the radical undergoes at least as favorable a solvation enthalpy change as does the hydroxylamine. For benzene and toluene the solvation enthalpy of transfer favors the radical by close to 900 cal/mol. Electron-withdrawing substituents appear to decrease the solvation advantage of **1** in aromatics.

An interpretation of these results, which is consistent with the kinetic studies,[1] is that the aromatics are able to solvate the nitroxide radical in some specific manner not available to alkanes and cyclohexene. This appears to be strong thermodynamic evidence for the ability of aromatics to solvate radicals. If the effect is smaller here than in some of the kinetic cases, this may be a reflection of the greater stability of the nitroxide.

Acknowledgment. This work was supported by a grant from the National Science Foundation (No. GP-7487).

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[3] C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, **73**, 1572 (1969).

[4] (a) Address correspondence to this author; (b) National Defense Education Act Fellow 1968–1969.

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The Conformation and Absolute Configuration of (−)-*trans*-Cyclooctene

Sir:

The dissymmetric nature of the molecule *trans*-cyclooctene has been discussed by Cope,[1] who has reported a probable absolute configuration as determined by chemical means, Moscowitz and Mislow,[2] who have discussed the absolute configuration from a theoretical viewpoint, and others. It has been previously noted that there are two nonsuperimposable enantiomorphs for each of the two possible conformations of *trans*-cyclooctene. These four possible spatial arrangements can be roughly described as differing from one another by rotations of the mean place of carbon atoms 8,1,2,3 (containing the double bond) and of the mean plane of carbon atoms 4,5,6,7 about axes approximately passing through atoms (8,3) and (4,7), respectively (Figure 1).

In order to distinguish among these four choices a single-crystal X-ray study of *trans*-dichloro[(−)-*trans*-cyclooctene][(+)-α-methylbenzylamine]platinum(II) (Figure 2), the complex used to effect the resolution of (±)-*trans*-cyclooctene,[3] was undertaken.

Crystals of this complex, kindly provided by the late Dr. A. C. Cope, were yellow needles which were first thought to be orthorhombic but later found to be monoclinic with a very strong tendency to twin and to be twisted around the needle axis. With considerable difficulty suitable untwinned crystals were found. The

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[1] A. C. Cope and A. S. Mehta, *J. Amer. Chem. Soc.*, **86**, 5626 (1964).

[2] A. Moscowitz and K. Mislow, *ibid.*, **84**, 4606 (1962).

[3] A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. van Auken, and H. J. S. Winkler, *ibid.*, **85**, 3276 (1963).

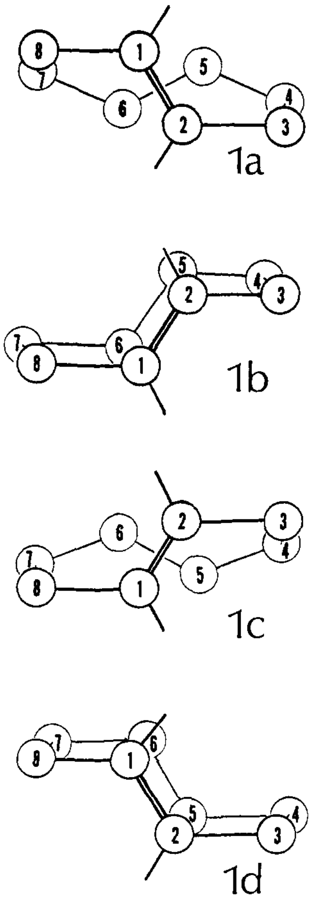

Figure 1. A rotation of the plane containing atoms 8, 1, 2, and 3 about a line connecting 8 and 3 gives **1b** from **1a**. **1c** may be obtained from **1b** by a rotation of the plane containing atoms 4, 5, 6, and 7 about a line connecting atoms 4 and 7. **1d** may be obtained from **1c** by a rotation of the plane containing atoms 8, 1, 2, and 3 about the line 8–3. **1a** is the mirror image of **1c**, and **1b** is the mirror image of **1d**.

lattice constants as determined on the diffractometer with Mo Kα radiation (λ 0.71070 Å) and refined by least squares are: $a = 11.94 \pm 0.01$, $b = 15.85 \pm 0.01$, $c = 9.45 \pm 0.01$ Å, $\beta = 90° 10' \pm 1'$. The only systematic extinctions were $0k0$, k odd, indicating space group $P2_1$. The observed density of 1.82 g/cm^3 obtained by flotation in aqueous thallous formate solution is consistent with the density 1.85 g/cm^3 calculated from the lattice constants and the molecular weight (497.38) assuming four molecules in the unit cell.

A total of 5775 intensity measurements were made with Zr-filtered Mo Kα radiation on a quarter-circle automatic diffractometer in the θ–2θ scan mode. The crystal was aligned in an arbitrary orientation in order to avoid systematic multiple diffraction but with the b axis of the crystal near the diffractometer's equatorial plane so that two complete quadrants related by Friedel mirror symmetry might be examined out to $2\theta = 45°$. Of the intensity measurements 74% were significantly above background; the 4283 observed reflections constituted 1851 pairs related only by Friedel mirror symmetry (which were averaged together for the initial work) and 581 others. Additionally, 12 check reflections were each measured on an average of about 50 times; during the course of the data collection these reflections showed declines in intensity ranging from 20 to 60%. Careful periodic checks of crystal alignment were made throughout the data collection. The results we report here are based on full-matrix least-squares refinement of all 4283 reflections corrected for absorption and corrected also with a curve representing the average time behavior of all check reflections.

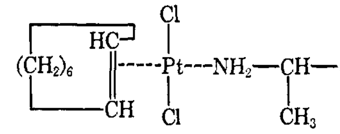

Figure 2. *trans*-Dichloro[(±)-*trans*-cyclooctene][(±)-α-methylbenzylamine]platinum(II).

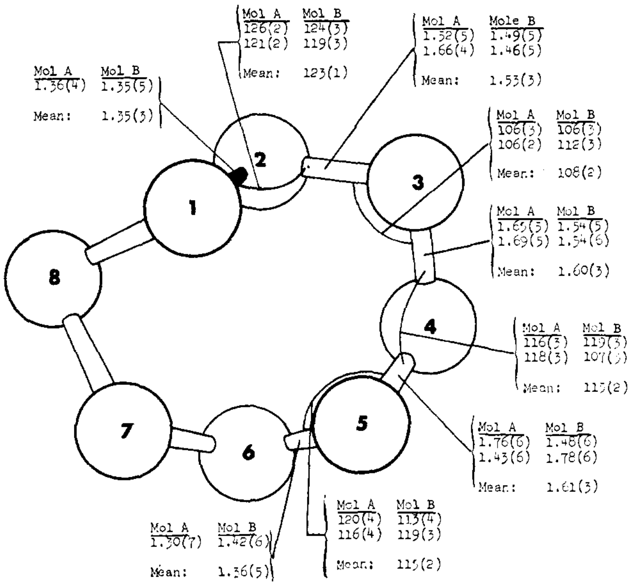

Figure 3. (−)-*trans*-Cyclooctene: conformation and configuration, with *apparent* interatomic distances and bond angles. For a given molecule, the upper of two values consistently represents the left side of the molecule; the lower one the right. Concerning deviations from "reasonable" limiting values, see text.

The platinum atoms were located from a sharpened Patterson map, and several subsequent electron density difference maps were necessary in order to locate the remaining 38 atoms of the asymmetric unit. Full-matrix least-squares refinement with the entire data set, including a correction for anomalous dispersion of platinum and chlorine, with isotropic temperature factors for C and N atoms and anisotropic temperature factors for Pt and Cl atoms, has led at this point to a conventional R index of 0.084.[4] Atomic form factors and dispersion corrections for Pt were taken from "International Tables for X-ray Crystallography;"[5] anomalous dispersion corrections for Cl ($\Delta f' = 0.168$, $\Delta f'' = 0.156$ electron) were obtained from Drs. Donald Cromer and David Liberman.[6]

Figures 3 and 1c show the conformation and absolute configuration found for the (−)-*trans*-cyclooctene moiety. The asymmetric unit contains two crystallographically nonequivalent (−)-*trans*-cyclooctene

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(4) We thank Professor James M. Stewart for supplying the X-Ray 67 Program System used for most of the computations, Drs. W. R. Busing, K. O. Martin, and H. A. Levy for the program OR-FLS used in the final refinement, and Drs. W. C. Hamilton and J. A. Ibers for the program PICK-2 used in cell constant and orientation refinement.

(5) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 202, 212, 215.

(6) D. T. Cromer and D. Liberman, VIIIth International Congress of Crystallography, Stony Brook, N. Y., Aug 1969.

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 $175.4 \pm 0.2°$.

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.

Acknowledgment. We are pleased to acknowledge the assistance of Dr. R. C. Srivastava in the early stages of the determination, and partial support of the work at that time by the National Institutes of Health.

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(7) W. C. Hamilton, K. A. Klanderman, and R. Spratley, *Acta Crystallogr., Sect. A*, **25**, 172 (1969).

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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, $[-\mathrm{d}(NO_2^-)/\mathrm{d}t]_t$, 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, $[+\mathrm{d}(O_2)/\mathrm{d}t]_t$, was determined by means of the automatic recording gas apparatus utilized in earlier studies.[9] A typical plot of the ratio $[-\mathrm{d}(NO_2^-)/\mathrm{d}t]_t/[+\mathrm{d}O_2/\mathrm{d}t]_t$ *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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(1) K. Gleu and P. Hubold, *Z. Anorg. Allg. Chem.*, **223**, 305 (1935).

(2) E. Halfpenny and P. L. Robinson, *J. Chem. Soc.*, 928 (1952).

(3) M. Anbar and H. Taube, *J. Amer. Chem. Soc.*, **76**, 6243 (1954).

(4) F. Bart, B. Hickel, and J. Sutton, *Chem. Commun.*, 125 (1969).

(5) U. Shuali, M. Ottolenghi, J. Rabani, and Z. Yelin, *J. Phys. Chem.*, **73**, 3445 (1969).

(6) M. Grätzel, A. Henglein, and S. Taniguchi, *Ber. Bunsenges. Phys. Chem.*, **74**, 292 (1970).

(7) W. G. Keith and R. E. Powell, *J. Chem. Soc. A*, 453 (1969).

(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.*

(9) L. R. Mahoney, R. W. Bayma, A. Warnick, and C. H. Ruof, *Anal. Chem.*, **36**, 2516 (1964).