consecutive reaction was not significant during the reaction time. Also, deliberate addition of $C_6H_5CH_2HgCl$ at the start of a run had essentially no effect on the rate, eliminating product catalysis as a source of the kinetic disturbance. Addition of HCl to CH_3CN was insignificant under these conditions.

We suspected that atmospheric oxygen was to blame for the situation. This was dramatically confirmed by data from runs conducted under a N_2 atmosphere. The consumption of HCl was now very slow, and virtually no disappearance of HCl occurred during the time when the reaction was previously essentially complete. Toward the end of a run medical air was admitted and the consumption of HCl was enormously accelerated. Clearly we are dealing with an oxygen-promoted reaction and protons, halide, and oxygen apparently form a very effective liason for cleavage of the mercurial.[11a] Under oxygen-free conditions, at 40°, the reaction between DBM and HCl correlates well with second-order kinetics for a satisfactory period before consecutive reactions intervene. The period of induction and erratic behavior under normal atmospheric conditions are the trademarks of radical-chain processes. Reactions between R_2Hg and O_2 are now well documented.[7,12]

This finding, coupled with that of Jensen,[7] has serious implications for other reported SE1 reactions of organomercurials. Thus we are disinclined to accept the report[13] of the "monomolecular protolysis of phenylmercuric bromide in 70% aqueous dioxane," and the reported SE1 protolysis of *trans*-ClCH=CHHgCl in DMSO[4] seems unreasonably rapid ($t_{1/2} \sim 9$ min at 20°), considering that such mercurials are prepared and are stable in 6 *N* HCl.[14] The reactions of ClCH=CHHgCl with both I_2[5] and HCl[4] in DMSO are reported to be of the SE1 type, implying identical rates for both reactions. However the iodine cleavage reportedly proceeds more rapidly at *20°* ($k_1 = 3.6 \times 10^{-3}$ sec^{-1}) than does the HCl protolysis at *30°* ($k_1 = 1.3 \times 10^{-3}$ sec^{-1}), suggesting some irregularity.

[11a] NOTE ADDED IN PROOF. The rate of reaction under aerobic conditions was at least 10^2 greater than that for the reaction under anaerobic conditions. A referee has kindly drawn our attention to a paper by M. M. Kreevoy and R. L. Hansen (*J. Phys. Chem.*, **65**, 1055 (1961)) who noted that the reactions of isopropyl- and *t*-butylmercuric iodides with perchloric acid were profoundly accelerated by oxygen with rate enhancements of *ca.* 10^2–10^3. Although the details of the aerobic reaction are not clear, oxygen insertion into the C–Hg bond may well be a key step in the sequence. Our chief concern was to demonstrate that the reaction was not of the SE1 type.

[12] See, for example, Yu. A. Aleksandrov, O. N. Druzhkov, S. F. Zhil'tsou, and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, **157**, 1395 (1964), and subsequent papers.

[13] I. P. Beletskaya, A. E. Myshkin, and O. A. Reutov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **2**, 240 (1965); see also ref 8.

[14] See, for example, A. N. Nesmeyanov and R. Kh. Freidlina, *Bull. Acad. Sci. USSR, Div. Chim. Sci.*, 150 (1945), and subsequent papers.

Brian F. Hegarty, William Kitching, Peter R. Wells
Department of Chemistry, University of Queensland
Brisbane, Australia

Received April 24, 196

Additions and Corrections

New Structural and Stereochemical Aspects of the Cyclization of Olefinic Acetals [*J. Am. Chem. Soc.*, **89**, 170 (1967)]. By WILLIAM S. JOHNSON, ARNE VAN DER GEN, and JOHANN J. SWOBODA, Department of Chemistry, Stanford University, Stanford, California 94305.

The following paragraph should be added at the end of the paper.

Acknowledgment. We thank the U. S. Public Health Service, the National Science Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Mechanisms of Photochemical Reactions in Solution. XLIV. Photodimerization of Cyclohexenone [*J. Am. Chem. Soc.*, **89**, 3482 (1967)]. By ERNEST Y. Y. LAM, DONALD VALENTINE, and GEORGE S. HAMMOND, Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California 91109.

On page 3483, column 2, the beginning of line 13 should read: enone concentration is 0.05 *M*.

Mechanisms of Reactions of Thiolsulfinates (Sulfenic Anhydrides). I. The Thiosulfinate–Sulfinic Acid Reaction [*J. Am. Chem. Soc.*, **89**, 3557 (1967)]. By JOHN L. KICE, CLIFFORD G. VENIER, and LESLIE HEASLEY, Department of Chemistry, Oregon State University, Corvallis, Oregon 97331.

On page 3559, eq 2b should read

$$(ArSO_2H)_{av} = (ArSO_2H)_0 - a(Ib)_0/2 \qquad (2b)$$

The Thiolochromium(III) Ion [*J. Am. Chem. Soc.*, **89**, 3661 (1967)]. By MICHAEL ARDON and HENRY TAUBE, Department of Chemistry, Stanford University, Stanford, California 94305.

On page 3662, column 1, line 13, $Cr(H_2O)_5Cl^{2+}$ should read $Cr(H_2O)_5I^{2+}$.

Steric Hindrance to the Formation of and Protonation of the Nitronate Ion from 2-Aryl-1-nitrocyclohexanes [*J. Am. Chem. Soc.*, **89**, 3906 (1967)]. By F. G. BORDWELL and MARTHA M. VESTLING, Department of Chemistry, Northwestern University, Evanston, Illinois 60201.

On page 3906, column 2, line 18, (axial) should read (equatorial).