oxidation of osmium and rhenium dinitrogen complexes,[5] led to the loss of dinitrogen in this case.

The $Mo(N_2)_2(arphos)_2$ complex was also oxidized by iodine,[4] hydrogen chloride, and hydrogen bromide. The infrared data are presented in Table I.

Table I. $\nu(N{\equiv}N)$ Stretching Vibration (cm^{-1}) for the Dinitrogen Complexes of Molybdenum(I) (Nujol Mull)

Starting complex	Oxidizing agent	$\nu(N{\equiv}N)$ of the product
$Mo(N_2)_2(diphos)_2$	I_2	2043 s
$Mo(N_2)_2(diphos)_2$	HCl	2047 s
$Mo(N_2)_2(diphos)_2$	HBr	2047 s
$Mo(N_2)_2(arphos)_2$	I_2	2043 s
$Mo(N_2)_2(arphos)_2$	HCl	2052 s
$Mo(N_2)_2(arphos)_2$	HBr	2052 s

(5) J. Chatt, J. R. Dilworth, H. P. Gunz, G. J. Leigh, and J. R. Sanders, *Chem. Commun.*, 90 (1970).

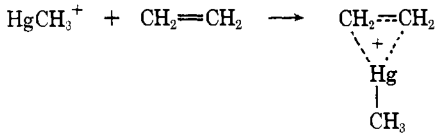
T. Adrian George,* C. D. Seibold
Department of Chemistry, The University of Nebraska
Lincoln, Nebraska 68508
Received June 24, 1972

The Observation of a Mercurinium Ion in the Gas Phase by Ion Cyclotron Resonance

Sir:

Mercurinium ions have been postulated as intermediates in the oxymercuration of olefins for many years.[1] However, unequivocal evidence for their involvement has not been reported and Brown[2] has recently discussed the unimportance of mercurinium ions in the oxymercuration of olefins. The first observation of a stable long-lived mercurinium ion was recently reported by Olah and Clifford.[3] They established, on the basis of nmr data, that mercurinium ions are stable in $FSO_3H\text{-}SbF_5\text{-}SO_2$ solvent at temperatures below −30°. We now report the first observation of a mercurinium ion in the gas phase.

The ionization of dimethylmercury at 3×10^{-6} Torr in an ion cyclotron resonance (icr) mass spectrometer (Varian Model ICR-9) with 25- and 40-eV electrons and in a cell at room temperature results in 34% Hg^+, 57% CH_3Hg^+, and 9% $CH_3HgCH_3^+$. The spectra were obtained by pulse electron beam modulation to give absorption type signals. When 4×10^{-6} Torr ethylene is added through a second inlet, a new ion is observed corresponding to the mass of $C_2H_4HgCH_3^+$. The new ion is attributed to the ethylene mercurinium ion **1** formed by the reaction shown in eq 1. The six mercury



$$HgCH_3^+ + CH_2{=}CH_2 \longrightarrow \underset{\substack{|\\CH_3}}{\overset{CH_2\text{---}CH_2}{\overset{\diagdown + \diagup}{Hg}}} \qquad (1)$$

1

isotopes from 198 to 204 amu are not resolved in the mercury containing ion peaks, but each broad peak is consistent with the mercury isotopic distribution. The ion peak assigned to **1** clearly contains one mercury, three carbons, and 7 ± 2 hydrogens. The intensity of **1** is linearly proportional to the ethylene pressure which is consistent with eq 1. Double resonance experiments[4] performed on $HgCH_3^+$ were inconclusive because there was insufficient resolution between the irradiating and observing frequencies and because the signal-to-noise ratio is small. However, double resonance experiments in which $C_2H_4^+$ was irradiated showed no effect on **1**; this indicates that formation of **1** does not occur by collision of $C_2H_4^+$ with dimethylmercury.

Under experimental conditions pertaining to the icr experiments, the ion resonance time is about 3×10^{-3} sec. Thus, the ion **1** is clearly stable for this period of time at room temperature. This is so much longer than typical metastable ion lifetimes ($\sim 10^{-5}$ sec) that we regard **1** as a truly stable gas-phase species.

We also wish to report, on the basis of molecular orbital calculations, that the most stable form of this ion is the symmetrically bridged ion **1**. The ion produced upon collision of $HgCH_3^+$ and ethylene could also exist as the unsymmetrical bridged ion **2** or the open classical ion **3**. Prior to Olah's report we had suggested[5] in a molecular orbital study of electrophilic additions to olefins that under suitable conditions mercurinium ions should be capable of independent existence. However, one of the difficulties with postulating the existence of onium ions on the basis of molecular orbital calculations is that the role of solvent in stabilizing charged species is difficult to ascertain. Our icr experiments clearly indicate that mercurinium ions are capable of existence in the absence of solvent.[6]

Extended Hückel[7] molecular orbital calculations were carried out and indicate that the symmetrical ion **1** is 1.9 kcal/mol lower in energy than the unsymmetrical ion **2**.[5] However, the classical ion **3**, with sp^2 hybridization at C_1 and sp^3 hybridization at C_2, is 41 kcal/mol less stable than the bridged ion **1**.[8] Thus, our calculations are in good agreement with experimental nmr evidence[3] where the importance of bridging in mercurinium ions in solution has been established.

(1) For a recent review of the oxymercuration reaction see W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968).

(2) H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, **93**, 7335 (1971).

(3) G. A. Olah and P. R. Clifford, *ibid.*, **93**, 1261, 2320 (1971).

(4) L. R. Anders, J. L. Beauchamp, R. C. Dunbar, and J. Baldeschwieler, *J. Chem. Phys.*, **45**, 1062 (1966).

(5) R. D. Bach and H. F. Henneike, *J. Amer. Chem. Soc.*, **92**, 5589 (1970).

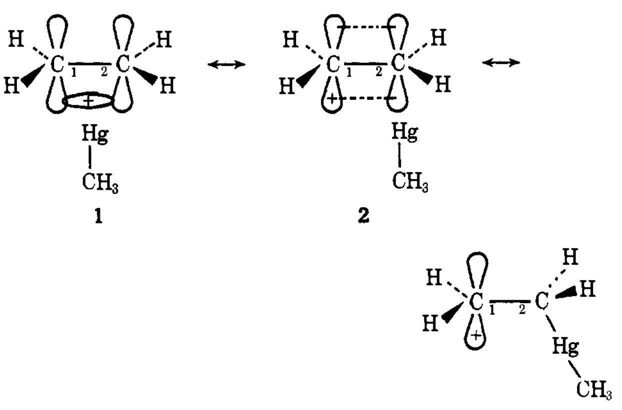
(6) We also have unequivocal evidence that $HgBr_2$ reacts reversibly with an olefin and an allene in the absence of solvent. *trans*-Cyclooctene was passed through a 2-ft 2% $HgBr_2$ on firebrick (no liquid phase was present) gas chromatograph column and was completely (>99.99%) isomerized to *cis*-cyclooctene at 40° (He gas ~ 50 cc/min). The trans olefin was also completely isomerized on a 2.5-ft 5% $HgBr_2$ and 10% SE-30 on firebrick. The trans olefin was 69% isomerized to *cis*-cyclooctene on a 1-ft column. In a control experiment, *trans*-cyclooctene was 1.4% isomerized on a 2.5-ft firebrick column. Optically active 1,2-cyclononadiene, $[\alpha]^{25}D$ −81°, was passed through a 2% $HgBr_2$ on firebrick column and was essentially completely racemized. The same results were obtained with the liquid phase (SE-30) present. These results are only consistent with a reversible equilibrium between the double bond and $HgBr_2$ (unpublished results with R. F. Richter).

(7) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963). For the method of calculation, the geometry and the parameters used in these calculations, see ref 5.

(8) A referee has suggested that rearrangement of **1** to a classical ethyl cation, $CH_3^+CHHgCH_3$, should be considered. However, EH calculations suggest that this rearrangement would be endothermic by ~160 kcal/mol. It is also significant that protonation of vinylmercurials in solution does not afford an ethyl cation intermediate.[9] Kinetic studies[10] suggest that an olefin–mercuric halide complex is the product of the rate-determining proton transfer to carbon, rather than a simple carbonium ion.

(9) I. P. Beletskaya, V. I. Karpov, V. A. Moskalenko, and O. A. Reutov, *Proc. Acad. Sci. USSR, Chem. Sect.*, **162**, 414 (1965).

(10) M. M. Kreevoy and R. A. Landholm, *Int. J. Chem. Kinet.*, **1**, 157 (1969).



1

2

3

The relatively low barrier for interconversion of **1** to **2** is also consistent with experimental[11] and theoretical[12] studies on the importance of carbon–metal σ–π conjugation in the stabilization of mercurinium ions.[13] The extent of perturbation of the double bond by $HgCH_3^+$ may be estimated by a comparison of the Mulliken overlap population for ethylene, $\rho_\pi = 0.503$, with that of the π system of the mercurinium ions **1**–**3**. The Mulliken overlap population for the C_1–C_2 π bond in **1** has been reduced to 0.368. In the unsymmetrical ion **2** this value is slightly increased to 0.381. The overlap population between the carbon 2p π orbital on C_1 and electron density on mercury is only 0.110 in **2**. Thus, 78% of the stabilization of the positive charge on C_1 in **2** is due to delocalization of the polarizable carbon–mercury σ bond and only 22% to neighboring group participation by mercury. With the classical ion **3** ρ_π is 0.346 and the overlap population between the neighboring group $HgCH_3$ and the π orbital on carbon, ρ_{C_1-Hg}, is reduced to 0.052. Thus, in **3** both σ–π conjugative stabilization and neighboring group participation are reduced. The increase in energy of **3** is also reflected in an increase in positive charge on C_1 which is 0.114, 0.123, and 0.177 for ions **1**, **2**, and **3**, respectively.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Institutes of Health (ES 00761-01) for support of this work.

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(11) T. G. Traylor, W. Hanstein, J. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, **93**, 5715 (1971).

(12) R. D. Bach and P. A. Scherr, *ibid.*, **94**, 220 (1972).

(13) T. G. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969).

Robert D. Bach,* Johannes Gauglhofer, Larry Kevan
Department of Chemistry, Wayne State University
Detroit, Michigan 48202

Received April 4, 1972

Activity Coefficient Effects in Spectral and Solubility Studies of Molecular Complex Equilibria

Sir:

Information about molecular complexes of iodine has played a key role in the development of theories of electron donor–acceptor interaction.[1] Yet, in spite of the importance of these adducts, there remains considerable disagreement regarding the magnitudes of spectral and thermodynamic constants of iodine complexes in nonpolar media.[1–6] When different physical methods are employed to study the same series of complexes, discrepancies are particularly large. For example, formation constant (K_c) values determined by the solubility method are as much as twice as great as those inferred from spectral techniques.[4,5]

It has been stated that the solubility method and similar thermodynamic techniques yield K_c values which account for the total effect of donor–acceptor interactions (specific plus nonspecific),[5b] whereas K_c values determined spectrally reflect only the effects of donor–acceptor contacts occurring in excess of random collisions.[7] This communication treats explicitly the effect of variation in activity coefficients on values of thermodynamic constants inferred from the solubility method and compares the corrected solubility results with constants determined spectrally.

Consider the reaction $D + I_2 \rightleftharpoons DI_2$ which occurs between dissolved donor (D) and iodine in dilute solution in a solvent (*e.g.*, heptane). The thermodynamic equilibrium constant for the reaction (in reciprocal molarity units) is

$$K_c = a_{DI_2}/(a_D a_{I_2}) = (c_{DI_2}/c_D c_{I_2})(\gamma_{DI_2}/\gamma_D \gamma_{I_2})$$

where a_i, c_i, and γ_i represent the activity, molar concentration, and activity coefficient of a solute species i (DI_2, D, or I_2). The activity coefficients are based on ideal dilute solution (unit molarity) standard states; the γ_i values individually approach unity as the total solute concentration approaches zero. In conventional spectral studies it is common to assume that $\gamma_{DI_2} \simeq \gamma_D \gamma_{I_2}$, even in treating data for quite concentrated solutions. This assumption has been criticized and defended by various workers.[8–10] At first glance, it would appear that constants derived from solubility results should be less influenced by activity coefficient effects, since meaningful measurements of solubility increases can be made in the very dilute solution range.[5] However, the total concentration of dissolved iodine, at constant activity in the presence of an added donor, can be expressed as

$$[I_2] = c_{I_2} + c_{DI_2} = (a_{I_2}/\gamma_{I_2}) + c_{DI_2} \tag{1}$$

where a_{I_2} is fixed and known.[11] As more donor is

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(1) For general references, see (a) R. S. Mulliken and W. B. Person, "Molecular Complexes. A Lecture and Reprint Volume," Wiley-Interscience, New York, N. Y., 1969; (b) R. Foster, "Organic Charge-Transfer Complexes," Academic Press, London and New York, 1969; (c) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1961.

(2) L. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.*, **79**, 4839 (1957).

(3) P. J. Trotter and M. W. Hanna, *ibid.*, **88**, 3724 (1966).

(4) G. Kortüm and W. M. Vogel, *Z. Elektrochem.*, **59**, 16 (1955); J. A. A. Ketelaar, C. Van de Stolpe, A. Goudsmit, and W. Dzcubas, *Recl. Trav. Chim. Pays-Bas*, **71**, 1104 (1952).

(5) (a) J. D. Childs, S. D. Christian, and J. Grundnes, *J. Amer. Chem. Soc.*, **94**, 5657 (1972); (b) J. D. Childs, Ph.D. Dissertation, The University of Oklahoma, 1971.

(6) R. L. Scott and D. V. Fenby, *Annu. Rev. Phys. Chem.*, 20, 111 (1969).

(7) R. L. Scott, *J. Phys. Chem.*, **75**, 3843 (1971).

(8) S. K. Alley and R. L. Scott, *ibid.*, **67**, 1182 (1963).

(9) Reference 1a, pp 91, 98–100.

(10) M. W. Hanna and D. G. Rose, *J. Amer. Chem. Soc.*, **94**, 2601 (1972).

(11) In the polyiodide solubility method, mixtures of tetramethylammonium polyiodides are utilized to maintain a constant activity of iodine in a solution phase or gaseous phase containing added donor.[5,12] Studies of aromatic donor–iodine complexes in heptane are conveniently performed by using tetramethylammonium triiodide and pentaiodide solid mixtures, which in contact with liquid heptane at 25° give an equilibrium concentration of molecular iodine equal to 1.97 × 10^{-4} *M*. In these experiments, $c_D \gg c_{I_2}$ or c_{DI_2}, which implies that activity coefficient effects in the solution phase are determined by the relative concentrations of heptane and donor.