67598-31-6; *trans*-$(C_2H_5)_4HMoOCl_2(sap)$, 67598-33-8; $MoO_2(ox)_2$, 17856-49-4; $MoO_2(tox)_2$, 17926-52-2; $MoO_2(mee)$, 67598-34-9; $MoO_2(mpe)$, 67598-35-0; $MoO_2(sap)$, 67598-36-1; MoO_2Cl_2, 13637-68-8; phen, 66-71-7; bpy, 366-18-7; $(NH_4)_2MoOCl_5$, 17927-44-5.

References and Notes

(1) R. C. Bray, *Enzymes*, **12**, 299 (1975).
(2) E. I. Stiefel, *Prog. Inorg. Chem.*, **22**, 1 (1977).
(3) J. T. Spence in "Metal Ions in Biological Systems", Vol. 5, H, Sigel, Ed., Marcel Dekker, New York, N.Y., 1976, p 273.
(4) G. D. Lawrence and J. T. Spence, *Biochemistry*, **14**, 3626 (1975); **16**, 3087 (1977).
(5) R. C. Bray, S. P. Vincent, D. J. Lowe, R. A. Clegg, and P. B. Garland, *Biochem. J.*, **155**, 201 (1976).
(6) J. T. Spence, M. Minelli, and P. Kroneck, submitted for publication.
(7) R. D. Taylor, P. G. Todd, N. D. Chasteen, and J. T. Spence, submitted for publication.
(8) A. F. Isbell, Jr. and D. T. Sawyer, *Inorg. Chem.*, **10**, 2449 (1971).
(9) J. K. Howie and D. T. Sawyer, *Inorg. Chem.*, **15**, 1892 (1976).
(10) L. J. DeHayes, H. C. Faulkner, W. H. Doub, Jr., and D. T. Sawyer, *Inorg. Chem.*, **14**, 2110 (1975).
(11) V. R. Ott and F. A. Schultz, *J. Electroanal. Chem. Interfacial Electrochem.*, **61**, 81 (1975).
(12) Abbreviations used for ligands: phen = *o*-phenanthroline; bpy = α,α'-bipyridyl; ox = 8-hydroxyquinoline; tox = 8-mercaptoquinoline; salphen = disalicylaldehyde *o*-phenylenediimine; mee = *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)ethylenediamine; mpe = *N,N'*-bis(2-mercapto-2-methylpropyl)ethylenedamine; sap = salicylaldehyde *o*-hydroxyanil.
(13) J. Enemark and K. Yamanouchi, private communication.
(14) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
(15) D. T. Sawyer and J. L. Roberts, Jr., "Experimental Electrochemistry for Chemists", Wiley, New York, N.Y., 1974, p 340.
(16) R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc. A*, 2632 (1969).
(17) G. J. J. Chen, J. W. McDonald, and W. E. Newton, *Inorg. Chem.*, **15**, 2612 (1976).
(18) J. S. Olson, D. P. Ballou, G. Palmer, and V. Massey, *J. Biol. Chem.*, **249**, 4363 (1974).
(19) H. Fleck and A. M. Ward, *Analyst (London)*, **58**, 388 (1933).
(20) K. D. Karlin and S. J. Lippard, *J. Am. Chem. Soc.*, **98**, 6951 (1976).
(21) J. L. Corbin and D. E. Work, *J. Org. Chem.*, **41**, 489 (1976).

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Mass Spectrometric Observation and Bond Dissociation Energy of Dimolybdenum, $Mo_2(g)$

S. K. GUPTA, R. M. ATKINS, and K. A. GINGERICH*

Received April 4, 1978

The diatomic molecule Mo_2 has been identified, and its thermodynamic properties have been studied in a high-temperature mass spectrometric experiment. From the partial pressures of Mo and Mo_2 measured as a function of temperature in the 2600–3000 K range, the dissociation energy of $Mo_2(g)$ was determined as $D°_{298} = 406 \pm 20$ kJ mol^{-1} or 97 ± 5 kcal mol^{-1}, and $D°_0 = 404 \pm 20$ kJ mol^{-1} or 96.5 ± 5 kcal mol^{-1}. The results are consistent with the trends predicted for the bond energies of diatomic molecules of group 5B and 6B elements in the first and second transition series by theoretical calculations.

Introduction

Currently, there is a great deal of interest in multiple metal–metal bonding in transition metals. An increasing number of theoretical as well as experimental studies of diatomic transition-metal molecules are appearing in the literature. This activity was initiated by the recent realization that a knowledge of the chemical and electronic properties of small transition- and noble-metal clusters is of fundamental importance to the understanding of the catalytic properties of transition metals. Diatomic molecules, or dimers, of a large number of transition metals have been characterized by Knudsen-cell effusion mass spectrometry[1,2] and other techniques such as matrix synthesis and isolation.[3] However, experimental studies of dimers of refractory metals, Nb, Mo, W, Pt, etc., either are lacking entirely or have been unsuccessful. This is presumably because severe experimental difficulties are encountered at the extremely high temperatures at which measurable pressures of the dimers would be obtained.

Very recently, the diatomic species Nb_2 and Mo_2 have been identified by quantitative UV–visible spectroscopy in matrix-condensation experiments by Ozin and co-workers.[3] Nevertheless, the need remains to determine their bond energies in order to establish trans-group and trans-transition series correlations of bonding characteristics of the homonuclear diatomics. The molecule Mo_2 is of particular interest. It is predicted to have the highest dissociation energy among the second transition series diatomic species. A bond order as high as 6 is indicated for Mo_2 from the results of extended Hückel molecular orbital[3] and SCF-Xα-SW[4] calculations. The present study was aimed at the detection and the measurement of the dissociation energy of gaseous Mo_2 under thermal equilibrium conditions.

Experimental Section

A single-focusing, 90° magnetic sector mass spectrometer (Nuclide, Model 12-90-HT) equipped with a Knudsen cell assembly was employed in this investigation. The instrument and the experimental procedures have been described previously[5,6] and only the details specific to this study will be discussed here.

The success of the experiment depended upon a right choice of the material for the Knudsen cell container. Since temperatures up to 3000 K were anticipated, the Knudsen-cell material had to meet two requirements: those of mechanical stability and nonreactivity with molybdenum metal so as not to lower its activity excessively. A tantalum Knudsen cell lined with a graphite cell, both with knife-edge orifices of 0.040-in. diameter, was charged with about 180 mg of niobium powder and heated to about 3000 K in the mass spectrometer. The purpose of this treatment was twofold: one, to coat the inside of the cell with a layer of highly refractory niobium carbides and two, to attempt observation of Nb_2.[7] A dramatic decrease in the ion currents due to carbon species (in fact, C_3 could no longer be detected) at about 2900 K indicated that all of the carbon of the inner cell had reacted with niobium and/or with the tantalum cell itself. The cell was then charged with fine cuttings of molybdenum foil (190 mg) along with a small amount of gold for pressure calibration purposes.

A 21-eV electron beam at a total emission of 0.3 mA was employed to ionize the Knudsen cell effusate. The ions were accelerated through a potential of 4.5 kV and were detected through a 20-stage π-type electron multiplier with Be–Cu dynodes. The potential at the multiplier shield was maintained at approximately −2000 V. Ion currents of Mo^+ (m/z 98) and Mo_2^+ (m/z 192) were measured as a function of temperature in the 2600–3000 K range. Ions were identified by

0020-1669/78/1317-3211$01.00/0 © 1978 American Chemical Society

Table I. Measured Intensities of Mo^+ and Mo_2^+ Ions at Various Temperatures

	multiplier anode current, A	
T, K	Mo^+	Mo_2^+
2772	4.731×10^{-9}	1.033×10^{-12}
2806	3.659×10^{-9}	4.820×10^{-13}
2836	3.343×10^{-9}	3.902×10^{-13}
2849	8.124×10^{-9}	1.744×10^{-12}
2851	8.011×10^{-9}	1.790×10^{-12}
2856	4.756×10^{-9}	6.886×10^{-13}
2911	1.009×10^{-8}	2.296×10^{-12}
2933	1.030×10^{-8}	1.951×10^{-12}
2963	1.009×10^{-8}	1.423×10^{-12}

their mass to charge ratio and isotopic distribution. The appearance potential for Mo_2^+ was determined to be 8.0 ± 1.0 eV. Total ion currents of Mo^+ and Mo_2^+ at various temperatures computed from the measured $^{98}Mo^+$ and $^{192}Mo_2^+$ currents are listed in Table I.

The sensitivity constant for the instrument was determined by measuring Au^+ and Au_2^+ ion currents in the 1500–1900 K temperature range. By combining the experimental currents with literature[8] data on the free-energy functions of Au(g) and Au_2(g) and the bond dissociation energy of gold dimer, a value of 1.34 ± 0.10 atm A^{-1} K^{-1} was obtained for the pressure constant of gold, k_{Au}. The pressure constants for Mo and Mo_2 were derived from the relation $k_i = k_{Au}(\sigma_{Au}\gamma_{Au}E_i/\sigma_i\gamma_iE_{Au})$, where σ, γ, and E are the ionization cross section, the multiplier gain, and the intensity correction factor, respectively. The multiplier gain for Mo^+ was measured to be $(1.25 \pm 0.10) \times 10^5$ and that for Au^+ to be $(7.76 \pm 0.05) \times 10^4$. Since, because of the small Mo_2^+ ion intensities, the gain for Mo_2^+ could not be experimentally measured, a simple approximation that $\gamma_{Mo_2^+} = \gamma_{Mo^+}$ was made. The approximation is supported by the findings of Liebl et al.[9] that at constant ion energy, the ratios of the secondary electron yield of the diatomic ion to that of the atomic ion for Si, Ni, and W are 1.26, 1.27, and 0.74, repectively. Also, Glick et al.[10] found, again at constant energy, the corresponding ratios to be nearly equal to 1.0 in the case of N and O. Thus $\gamma_{Mo^{2+}} = (1.25 \pm 0.25) \times 10^5$ would be a reasonable estimate. The ionization cross sections for the atoms used are from Mann.[9] The cross section for Mo_2 was taken to be 1.5 times that of Mo. Thus the values $k_{Mo} = 0.65 \pm 0.10$ atm A^{-1} K^{-1} and $k_{Mo_2} = 0.43 \pm 0.07$ atm A^{-1} K^{-1} were determined.

Results and Discussion

Absolute partial pressures of Mo(g) and Mo_2(g), calculated from the corresponding ion currents listed in Table I through the relation $p = kI^+T$, are given in Table II. Second- and third-law methods were employed to determine the enthalpy of the dissociation reaction $Mo_2(g) = 2Mo(g)$.

The second-law plot of ln K_p vs. $1/T$ shown in Figure 1 yields $\Delta H°_{T_{mean}} = (-R \times \text{slope}) = 424.5 \pm 33.3$ kJ mol^{-1}, where $T_{mean} = 2864$ K corresponds to the mean of $1/T_{max}$ and $1/T_{min}$. Also from this plot, $\Delta S°_{2864} = (R \times \text{intercept } (y \text{ axis})) = 129.4 \pm 11.6$ J mol^{-1} K^{-1}. In the third-law method, $\Delta H°_{298} = -RT \ln K_p - T\Delta[(G°_T - H°_{298})/T]$ at each temperature of measurement, where $\Delta[(G°_T - H°_{298})/T]$ is the change in the free-energy function for the reaction. The necessary free-energy functions, $(G°_T - H°_{298})/T$, and the heat-content functions, $H°_T - H°_{298}$, needed for computing $\Delta H°_{298}$ (second law) were taken from the literature in the case of Mo(g),[12] while for Mo_2(g) they were computed from molecular parameters using standard statistical thermodynamic expressions. The Mo–Mo distance, r_e, was taken as 2.12 Å, the value arrived at by Ozin et al.[3] and by Norman et al.[4] from theoretical considerations. The former workers have also reported a tentative value for the fundamental vibrational frequency of Mo_2, $\omega_e = 315$ cm^{-1} from Raman spectroscopy. The thermodynamic functions at various temperatures for Mo_2 on the basis of the above parameters are listed in Table III. In accordance with the closed-shell configuration corresponding to sextuple bond formation in Mo_2 indicated by MO calculations, electronic contributions to the free-energy functions of Mo_2 were assumed to be zero (neglecting any possible contribution from excited states).

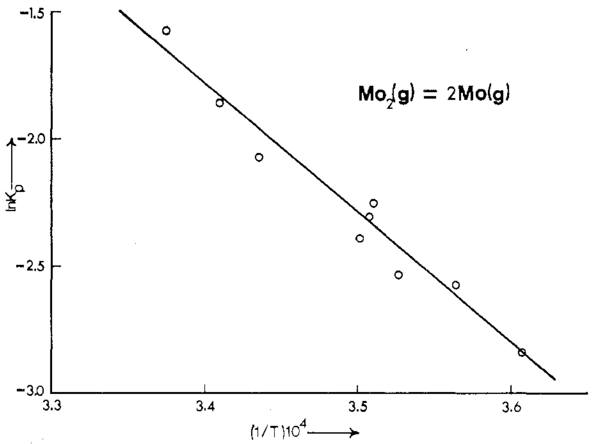

Figure 1. Second-law plot of the reaction $Mo_2(g) = 2Mo(g)$.

A summary of third-law evaluations is presented in Table II. The second-law values of $\Delta H°_{298} = 409.0 \pm 33.3$ kJ mol^{-1} and $\Delta S°_{298} = 117.5 \pm 11.6$ J mol^{-1} K^{-1} are in good agreement with the corresponding third-law values, 403.8 ± 1.8 kJ mol^{-1} and 115.7 J mol^{-1} K^{-1}, respectively. The small discrepancy between the two may reflect the scatter of the experimental quantities or incorrect free-energy functions for Mo_2(g). In fact, if for Mo_2 a value of $\omega_e = 418$ cm^{-1} calculated from Guggenheimer's relation[13] is used, the third-law values become $\Delta H°_{298} = 410.2 \pm 1.8$ kJ mol^{-1} and $\Delta S°_{298} = 117.5$ J mol^{-1} K^{-1}. We select as final values $\Delta H°_{298} = 406 \pm 20$ kJ mol^{-1} or 97 ± 5 kcal mol^{-1} and $\Delta S°_{298} = 117 \pm 5$ J mol^{-1} K^{-1} or 28.0 ± 1.2 cal mol^{-1} K^{-1} by averaging the third-law values based on $\omega_e = 315$ cm^{-1} with the corresponding second-law values. The error limits on the final values were estimated to include uncertainties due to all possible errors.

The bond dissociation energy of Mo_2 determined in this work is in agreement with the trend found for the first- and second-row transition-metal cluster compounds[14] in that it is higher than the bond dissociation energies of the first-row transition-metal diatomics V_2[15] ($D°_0 = 240.6 \pm 12.6$ kJ mol^{-1}) and Cr_2[16] ($D°_0 = 150.6 \pm 29.3$ kJ mol^{-1}). The large difference

Table II. Partial Pressures of Mo(g) and Mo_2(g) and the Summary of Third-Law Calculations for the Reaction $Mo_2(g) = 2Mo(g)$[a]

T, K	$10^6 p_{Mo}$, atm	$10^{10} p_{Mo_2}$, atm	$\ln K_p(T)$	$-\Delta[(G°_T - H°_{298})/T]$, J mol^{-1} K^{-1}	$\Delta H°_{298}$, kJ mol^{-1}
2772	8.524	12.40	−2.8370	121.07	403.6
2806	6.674	5.856	−2.5764	121.14	402.7
2836	6.162	4.792	−2.5351	121.21	406.2
2849	15.04	21.51	−2.2519	121.24	401.4
2851	14.85	22.10	−2.3051	121.24	403.0
2856	8.829	8.516	−2.3910	121.25	405.7
2911	19.09	28.94	−2.0719	121.39	406.2
2933	19.64	24.78	−1.8603	121.44	404.2
2963	19.43	18.26	−1.5759	121.52	401.5

[a] $\Delta S°_{298} = 115.7$ J mol^{-1} K^{-1}, $\Delta S°_0 = 106.7$ J mol^{-1} K^{-1}; $\Delta H°_{298} = 403.8 \pm 1.8$ kJ mol^{-1}, $\Delta H°_0 = 401.2 \pm 1.8$ kJ mol^{-1}.

Table III. Free-Energy Functions in J mol^{-1} K^{-1} and Heat-Content Functions in kJ mol^{-1} for $Mo_2(g)^a$

T, K	$-(G°_T - H°_{298})/T$	$H°_T - H°_{298}$
298.15	247.98	0.00
2400	292.67	78.24
2500	294.01	81.98
2600	295.30	85.72
2700	296.54	89.46
2800	297.75	93.20
2900	298.92	96.94
3000	300.06	100.68

[a] $H°_{298} - H°_0 = 9.73$ kJ mol^{-1}.

in the bond energies of Cr_2 and Mo_2 is, however, surprising, especially since their optical spectra suggest that the electronic configurations and bonding interactions in Cr_2 and Mo_2 are similar.[3] Moreover, the three known dissociation energies, $D(V_2)$, $D(Cr_2)$, and $D(Mo_2)$, are in nonconformity with the trend indicated by MO calculations[3] that $D(Mo_2) > D(Cr_2) > D(Nb_2) > D(V_2)$. It is clear that an experimental determination of the dissociation energy of Nb_2 is needed in order to gain insight into the bonding properties of these diatomic molecules.

Acknowledgment. This work has been supported by the National Science Foundation under Grant No. CHE75-10075A01 and by the Robert A. Welch Foundation.

Registry No. Mo^+, 16727-12-1; Mo_2^+, 67891-04-7; Mo_2, 12596-54-2; Mo, 7439-98-7.

References and Notes

(1) K. A. Gingerich, *J. Cryst. Growth*, **9**, 31 (1971).
(2) G. De Maria and G. Balducci, *MTP Int. Rev. Sci.: Phys. Chem., Ser. One*, **10**, 209 (1972).
(3) W. Klotzbücher and G. A. Ozin, *Inorg. Chem.*, **16**, 984 (1977), and ref 1–5 therein.
(4) J. G. Norman, Jr., H. J. Kolari, H. B. Gray, and W. C. Trogler, *Inorg. Chem.*, **16**, 987 (1977).
(5) K. A. Gingerich, *J. Chem. Phys.*, 49, 14 (1968).
(6) D. L. Cocke and K. A. Gingerich, *J. Phys. Chem.*, **75**, 3264 (1971).
(7) Unfortunately, at the high temperatures where it was hoped that Nb_2 would be detected, the vapor pressure of tungsten (^{186}W) from the Knudsen-cell heater filament was high enough to obscure any Nb_2^+ signal at $m/z = 186$.
(8) J. Kordis, K. A. Gingerich, and R. J. Seyse, *J. Chem. Phys.*, **61**, 5114 (1974).
(9) G. Staudenmaier, W. O. Hofer, and H. Liebl, *Int. J. Mass Spectrom. Ion Phys.*, **21**, 103 (1976).
(10) M. Van Gorkom and R. E. Glick, *Int. J. Mass Spectrom. Ion Phys.*, **4**, 203 (1970).
(11) J. B. Mann, *Recent Dev. Mass Spectrosc., Proc. Int. Conf. Mass Spectrosc.* 814–819 (1970).
(12) R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley, and D. D. Wagman, "Selected Values of the Thermodynamic Properties of the Elements", American Society for Metals, Metals Park, Ohio, 1973.
(13) K. M. Gugenheimer, *Proc. Phys. Soc., London*, **58**, 456 (1946).
(14) F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975).
(15) A. Kant and S. S. Lin, *J. Chem. Phys.*, **51**, 1644 (1969).
(16) A. Kant and B. Strauss, *J. Chem. Phys.*, **45**, 3161 (1966).

Contribution from the Department of Chemical Engineering,
University of Waterloo, Waterloo, Ontario, Canada

Hydrogen Reduction of μ_3-Oxo-triruthenium(III) Acetate in Dimethylformamide

S. A. FOUDA, B. C. Y. HUI, and G. L. REMPEL*

Received September 1, 1977

μ_3-Oxo-triruthenium(III) acetate exists in dimethylformamide as a weakly dissociated 1:1 electrolyte, $[Ru_3O(OCOCH_3)_6(DMF)_3][OCOCH_3]$, with $K_{diss} = 8 \times 10^{-4}$ M at 30 °C. $[Ru_3O(OCOCH_3)_6(DMF)_3][OCOCH_3]$ undergoes three sequential reduction reactions with molecular hydrogen in DMF at 80 °C. The first reduction reaction involves consumption of 1 mol of hydrogen/mol of oxotriruthenium(III) acetate and results in the formation of 1 mol of an intermediate ruthenium hydride and 1 mol of acetic acid. A detailed mechanistic study for this first stage of reduction indicates that a monohydridic triruthenium species, $[HRu_3O(OCOCH_3)_5(DMF)_3][OCOCH_3]$, is formed via a heterolytic splitting of hydrogen by $[Ru_3O(OCOCH_3)_6(DMF)_3][OCOCH_3]$. The monohydride species undergoes a subsequent intramolecular reduction to produce the species $[Ru_3O(OCOCH_3)_4(DMF)_n][OCOCH_3]$ and an additional mole of acetic acid per mole of intramolecular reduction product. This intramolecular reduction product activates hydrogen in the second reduction reaction which involved consumption of 2 mol of H_2/mol of $[Ru_3O(OCOCH_3)_4(DMF)_n][OCOCH_3]$ and results in the production of an additional 2 mol of acetic acid and dimeric ruthenium(I) species. The activation appears to involve the formation of a three-centered intermediate between molecular hydrogen and one of the ruthenium centers of $[Ru_3O(OCOCH_3)_4(DMF)_n][OCOCH_3]$. This three-centered species gives rise to a heterolytic splitting of hydrogen. The consumption of the second mole of hydrogen during the second stage of reduction occurs rapidly and results in the formation of ruthenium(I) products. Decarbonylation of DMF occurs during the second stage of reduction and/or isolation of the solid ruthenium(I) products. The dimeric ruthenium(I) species are isolated from the DMF solution as a mixture of $Ru_2(OCOCH_3)_2(CO)_4L_2$ ($L = P(C_6H_5)_3$, $P(C_6H_5)_2(C_2H_5)$, $Sb(C_6H_5)_3$, C_5H_5N) and the novel compound $Ru_2(OCOCH_3)_2(HOCOCH_3)(CH_3OH)$. The DMF solution containing the dimeric ruthenium(I) species is found to undergo further reaction with hydrogen. The final products of the overall reaction are isolated as a mixture of $Ru_2(OCOCH_3)_2(CO)_4L_2$ and the polymeric hydridoruthenium carbonyl $[HRu(CO)_3]_n$.

Introduction

Although the chemistry of oxotriruthenium(III) acetate, $[Ru_3O(OCOCH_3)_6(H_2O)_3][OCOCH_3]$, in aqueous and methanolic media has been extensively investigated,[1-3] no information on its behavior or reduction chemistry in dimethylformamide has previously been reported. Previous investigations[1-3] indicate that trimeric complexes resulting from the hydrogen or electrochemical reduction of $[Ru_3O(OCOCH_3)_6(H_2O)_3][OCOCH_3]$ in water or methanol were not active as hydrogenation catalysts. Since $[Ru_3O(OCOCH_3)_6(H_2O)_3][OCOCH_3]$, when treated with H_2 in dimethylformamide, has been found to be effective in providing homogeneous catalysts for a variety of unsaturated substrates,[4] we have carried out a detailed study of its solution chemistry and hydrogen reduction in dimethylformamide. The objective of this study was primarily aimed at gaining further insight into the nature of oxotriruthenium acetate and the hydrogenation catalysts or catalyst precursors in DMF.

Experimental Section

Ruthenium trichloride trihydrate was obtained from Engelhard Industries Ltd. Reagent grade chemicals and solvents were used throughout. Dimethylformamide was purified by storing over CaH_2 under N_2 for at least 40 h followed by distillation under reduced pressure; the constant-boiling fraction was collected onto Linde 4A

0020-1669/78/1317-3213\$01.00/0