lar orbitals of the ionized molecule are those of the parent molecule. Electronic relaxation (*i.e.*, change of orbitals) in the ionized molecule or a difference in correlation energies (not included in SCF–MO treatment) will invalidate Koopmans' theorem. Thus a difference in electronic relaxation energies for photoionization of the e_{2g} electron as compared to the a_{1g} electron or a difference in correlation energy differences is the probable cause of this disagreement.

It would be interesting to have photoelectron ionization data for other metallocenes. The ligand field treatment of ruthenocene[1] gave $\Delta\epsilon^{\text{core}}(a_{1g}-e_{2g}) = -6600$ cm^{-1} and $B = 260$ cm^{-1}. In this case we would predict $\Delta\epsilon^{\text{SCF}}(a_{1g}-e_{2g}) \cong +1400$ cm^{-1}, and, if the collapse of Koopmans' theorem is no more extensive in ruthenocene, the ionization potentials of the ruthenocene 4d a_{1g} and e_{2g} electrons should be closer in energy than those for the ferrocene 3d electrons.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS 61801
DAVID N. HENDRICKSON

RECEIVED JUNE 4, 1971

On the Exchange of Oxygen between Sulfate and Water

Sir:

A good deal of conflicting data on the rate and mechanism of oxygen exchange between sulfate and water has been reported;[1] for example, the exchange in 1 *N* NaOH at 100° has been reported to be as great as 85% in 26 hr[1a] and as little as <1% in 456 hr.[1d]

More recently, Hoering and Kennedy[2] reported some experiments on the acid-catalyzed exchange of oxygen between sulfuric acid and water. The results of these experiments, coupled with earlier reports (*e.g.*, ref 1a), suggest that there may be a change in the exchange mechanism from acid-catalyzed dehydration to, for example, nucleophilic displacement by H_2O and/or OH^- at higher pH values. We wish to report a reinvestigation of this question using ^{18}O-labeled sulfate (91.9 atom % excess obtained from Miles-Yeda Ltd.).

In these experiments solutions of 0.1 *M* $Na_2S^{18}O_4$ were incubated at 100° for 63 days in Teflon bombs, either with no additions of in the presence of 1 *N* NaOH. A 0.1-ml aliquot of the incubated solution was then introduced with a syringe into an evacuated 5-ml stoppered serum vial containing sufficient $NaHCO_3$ to produce 5 ml (at STP) of CO_2 upon acidification. An excess of 85% lactic acid (0.05 ml) was then added to release the CO_2. (The small dilution of ^{18}O label due to H_2O–lactic acid oxygen exchange was accounted for in the calculation of exchange rates.) After an equilibration time of 18 hr at room temperature (sufficient for complete isotopic equilibration[3]), the CO_2 was introduced into a modified CEC isotope ratio mass spectrometer through a syringe–needle inlet and the $^{18}O:^{16}O$ ratio of the CO_2 determined (at *m/e* 46 and 44). Preliminary experiments showed that, under the conditions used for equilibration with CO_2, no exchange of ^{18}O between the sulfate and water occurred. Therefore, it was not necessary to separate the water from the salt solutions before analyses.

Four readings were made on each of three replicates for each experimental condition. Measurements of "standard CO_2" (derived from $NaHCO_3$ in the same manner) were interspersed between experimental measurements to detect and correct for any drift in the mass spectrometer readings. Preliminary experiments using $H_2{}^{18}O$ indicated that we could reliably detect an exchange of 0.1% under the conditions employed.

These experiments showed that under neutral or alkaline conditions (1 *N* NaOH), no exchange (<0.1%) occurred at 100° in 63 days. This suggests that the second-order rate constant (k_2) is $<1 \times 10^{-11}$ M^{-1} sec^{-1} using H_2O as a nucleophile. Similarly, using OH^- as a nucleophile, the second-order rate constant (k_2) is $<8 \times 10^{-10}$ M^{-1} sec^{-1}. By way of comparison, we find $k_2 = 5.3 \times 10^{-5}$ M^{-1} sec^{-1} for the acid-catalyzed exchange reaction at 100°, a value in good agreement with the value calculated from the data in ref 2. It thus appears that sulfate oxygen does not undergo appreciable exchange with the oxygen of H_2O by any mechanism other than acid-catalyzed dehydration under these conditions.

Acknowledgment.—This work was supported by the National Aeronautics and Space Administration under Contract NASw-2109.

BIOSCIENCES DEPARTMENT
RESEARCH INSTITUTE FOR ADVANCED STUDIES
BALTIMORE, MARYLAND 21227
RICHARD RADMER

RECEIVED OCTOBER 4, 1971

---

(1) (a) S. C. Datta, J. N. E. Day, and C. K. Ingold, *J. Chem. Soc.*, 1968 (1937); (b) G. A. Mills, *J. Amer. Chem. Soc.*, **62**, 2833 (1940); (c) N. F. Hall and O. R. Alexander, *ibid.*, **62**, 3455 (1940); (d) E. R. S. Winter, M. Carlton, and H. V. A. Briscoe, *J. Chem. Soc.*, 131 (1940); (e) E. R. S. Winter and H. V. A. Briscoe, *ibid.*, 631 (1942).

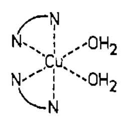
(2) T. C. Hoering and J. W. Kennedy, *J. Amer. Chem. Soc.*, **79**, 56 (1957).

(3) M. Cohn and H. C. Urey, *ibid.*, **60**, 679 (1938).

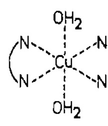
On the Observation of *cis*- and *trans*-Bis(2,2'-bipyridyl)copper(II) by Electron Spin Resonance

Sir:

Several recent investigations of bis(2,2'-bipyridyl)copper(II), $[Cu(bipy)_2(OH_2)_2]^{2+}$, have been concerned with the existence and relative stability of the two possible geometrical isomers of this complex: one in which the two water molecules are cis to each other and the other in which they are trans.[1–3]



cis



trans

Among these investigations is the comprehensive nmr and esr study of Noack and Gordon[1] of the Cu^{2+}–

---

(1) M. Noack and G. Gordon, *J. Chem. Phys.*, **48**, 2689 (1968).

(2) C. K. Jørgenson, *Acta Chem. Scand.*, **9**, 1362 (1955).

(3) Y. I. Skurlatov and A. P. Purmal, *Russ. J. Phys. Chem.*, **43**, 880 (1969).