rium is involved between a carbonyl of cobalt (possibly dicobalt octacarbonyl or the hydrocarbonyl), carbon monoxide and the olefin, the latter being able to substitute for some of the CO in the carbonyl. One possible scheme for the reaction is

$$[Co(CO)_4]_2 + C_6H_{10} \rightleftarrows \underset{(A)}{[Co_2(CO)_7C_6H_{10}]} + CO \qquad (1)$$

$$2Co(CO)_7C_6H_{10} + 2H_2 \longrightarrow 2C_6H_{11}CHO + [Co(CO)_3]_4 \qquad (2)$$

$$[Co(CO)_3]_4 + 4CO \rightleftarrows 2[Co(CO)_4]_2 \qquad (3)$$

It is possible that the postulated intermediate (A) is formed from the decomposition of the complex $[Co(CO)_4 \cdot olefin]^+[Co(CO)_4]^-$ recently suggested by Orchin[3] but further work is required, especially since the above tentative scheme does not assign a role to the hydrocarbonyl.

(3) M. Orchin, in "Advances in Catalysis," Vol. V, Academic Press, Inc., New York, 1953, p. 407.

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POLYATOMIC SPECIES IN SILVER VAPOR[1]

Sir:

Calculation of the molecular weight of silver vapor from the measured vapor velocity[2] and success of the famous Stern–Gerlach experiment in yielding in an inhomogeneous field the splitting predicted for a beam of silver atoms[3] apparently established beyond doubt that silver vapor is monoatomic at low pressures. We have found, however, a high concentration of polyatomic species in silver vapor at $\sim 10^{-6}$ to 10^{-4} atm. pressure.

By use of a method developed by Mayer[4] and Volmer,[5] we have measured the apparent molecular weight of silver vapor in a graphite box containing two small holes.

Pressure inside the box can be calculated from the hole areas, rate of weight loss due to escaping vapor, temperature and the molecular weight of the vapor by use of Knudsen's equation.[6] The pressure can also be calculated from the angle ϕ through which the force of the escaping vapor causes the box to rotate about a wire of torsion constant D. The equation used is $P = 2D\phi/(q_1a_1 + q_2a_2)$, where a_1 and a_2 are the areas of the holes and q_1 and q_2 are distances from the axes of the holes to the wire. Simultaneous solution of the equations yields the molecular weight M of the vapor.

Fifteen determinations at 1310 to 1420°K. gave $M = 278$ (2.56 times the atomic weight) with an estimated maximum uncertainty of ±90. This high average molecular weight cannot arise from systematic error because concurrent determinations of the molecular weights of tin[7] and germanium[8] vapors yielded values within estimated error of the atomic weights.

The existence of polyatomic ionic species in the vapor of silver metal was recently established through direct observation of the ions in a 60° single direction focusing mass spectrometer of very high sensitivity. In one run at various temperatures above the melting point and below 1500° silver vapor was found to contain ionic species (presumably formed by thermal ionization) corresponding to the compositions Ag^+, Ag_2^+, Ag_3^+ and Ag_4^+ in approximate relative intensities 15:7:30:1, respectively.

Identification of these species was made on the basis of the mass numbers observed, which were known from magnetic field calibration with a proton resonance fluxmeter, and on the basis of a characteristic mass spectrum for each species which results from the isotopic composition of silver. It has not been possible as yet to search for higher polymers which may also exist.

There is, of course, considerable uncertainty associated with the extension of these data to the relative abundances of neutral polyatomic species in the vapor state, but it may be noted that the above relative intensities would give an average molecular weight for silver vapor in good agreement with the above molecular weight determination.

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(1) Supported in part by the Office of Naval Research and in part by the Atomic Energy Commission.

(2) O. Stern, *Z. Physik*, **3**, 417 (1920).

(3) W. Gerlach and O. Stern, *ibid.*, **9**, 349 (1922).

(4) H. Mayer, *ibid.*, **67**. 240 (1931).

(5) M. Volmer, *ibid.*, *Chem.*, *Bodenstein Festband*, 863 (1931).

(6) M. Knudsen, *Ann. Physik*, [4] **28**, 999 (1909).

(7) A. W. Searcy and R. D. Freeman, THIS JOURNAL, in press.

(8) A. W. Searcy and R. D. Freeman, unpublished data.

MICROBIOLOGICAL TRANSFORMATIONS OF STEROIDS. XII.[1] 17α-HYDROXYLATION

Sir:

Preceding publications from our own as well as other laboratories have been concerned with the microbiological oxygenation of the steroid molecule at various positions of the skeleton. The introduction of a hydroxyl group into positions 6β,[2,3] 7β,[2,4] 8ξ,[2] 11α,[1,2,3,5,6] 11β,[2,7,8,9] 14α,[2,10] 15,[11] and 16α,[12,13] by the action of various genera of the filamentous fungi has been described. In some instances a simultaneous introduction of two hy-

(1) Paper XI of this series, THIS JOURNAL, in press.

(2) H. C. Murray and D. H. Peterson, U. S. Patent 2,602,769 (July 8, 1952).

(3) Papers III, IV, V, IX, and X of this series, THIS JOURNAL, **75**, 408, 412, 416, 5768 (1953); **76**, 3174 (1954).

(4) F. W. Kahnt, *et al.*, *Experientia*, **8**, 422 (1952).

(5) See, besides ref. 3, also papers I, II, VI and VII of this series, THIS JOURNAL, **74**, 5933 (1952); **75**, 55, 419, 421 (1953).

(6) J. Fried, *et al.*, *ibid.*, **74**, 3962 (1952).

(7) D. R. Colingsworth, *et al.*, *ibid.*, **74**, 2381 (1952); *J. Biol. Chem.*, **203**, 807 (1953).

(8) F. R. Hanson, *et al.*, THIS JOURNAL, **75**, 5369 (1953).

(9) G. M. Shull, D. A. Kita and J. W. Davisson, U. S. Patent 2,658,023 (Nov. 3, 1953).

(10) P. D. Meister, *et al.*, Abstracts of the 123rd Meeting of the American Chemical Society, Los Angeles, Calif., March 15–19 (1953), page 5C.

(11) (a) Personal communication from Dr. J. Fried, The Squibb Institute for Medical Research, New Brunswick, N. J.; (b) unpublished results, these laboratories.

(12) D. Perlman, E. Titus and J. Fried, THIS JOURNAL, **74**, 2126 (1952).

(13) E. Vischer, J. Schmidlin and A. Wettstein, *Helv. Chim. Acta*, **37**, 321 (1954).