acid suggests the presence of a hindered N-acetyl group (barring rearrangement). Thus oxonitine with methanolic · HCl yielded a basic and a neutral fraction. From the latter was isolated a substance (I) which results from the replacement of the acetoxy group by a methoxyl group; m.p. 265–268°, $[\alpha]^{29}\mathrm{D}$ −49° (c 0.47 in chf.). Calcd. for $C_{33}H_{45}NO_{11}$: C, 62.74; H, 7.18; OCH_3, 24.56. Found: C, 62.84, 62.70; H, 7.46, 7.09; OCH_3, 24.07, 23.91. On saponification 16.115 mg. consumed 0.21 ml. of 0.1 N NaOH; calcd. for 1 equiv., 0.25 ml.

The basic fraction yielded a secondary base (II)[4] formed by the loss of the N-acetyl group from I, m.p. 248–249°, $[\alpha]^{29}\mathrm{D}$ +33° (c 0.5 in chf.) Calcd. for $C_{31}H_{43}NO_{10}$: C, 63.14; H, 7.35; N, 2.38. Found: C, 62.87; H, 7.28, N. 2.61. Its N-nitroso derivative formed microplatelets, m.p. 246–248.5°. Calcd. for $C_{31}H_{42}N_2O_{11}$: C, 60.18; H, 6.84; N, 4.53. Found: C, 60.18, H, 6.78, N, 4.50. 15.175 mg. on saponification consumed 0.228 ml. of 0.1 N NaOH; calcd. for 1 equiv., 0.249 ml.

Treatment of I with Ac_2O gave a mixture from which was isolated a compound (III) containing an extra O-acetyl group, m.p. 290–296°, $[\alpha]^{29}\mathrm{D}$ −56° (c 0.18 in chf.). Calcd. for $C_{35}H_{47}NO_{12}$: C, 62.39; H, 7.03. Found: C, 62.11; H, 6.92. A substance indistinguishable from III was obtained by acetylation of base II, m.p. 291–297°, $[\alpha]^{30}\mathrm{D}$ −56° (c 0.5 in chf.). No m.p. depression was observed. Found: C, 62.20; H, 7.00.

Treatment of oxoaconitine with methanolic HCl also yielded basic and neutral fractions. From the latter a substance (IV) was isolated which results from loss of a mole of methanol but with retention of the acetoxy group, m.p. 271–273.5°, $[\alpha]^{28}\mathrm{D}$ +22° (c 1.03 in chf.). Calcd. for $C_{33}H_{39}NO_{11}$: C, 63.35; H, 6.28; OCH_3, 14.88. Found: C, 63.24; H, 6.17; OCH_3, 14.59.

From the basic fraction a secondary base (V) melting at 180–185° was obtained, $[\alpha]^{28}\mathrm{D}$ + 69° (c 0.51 in chf.). Calcd. for $C_{31}H_{37}NO_{10}$: C, 63.79; H, 6.39; OCH_3, 15.95. Found: C, 63.55; H, 6.27; OCH_3, 16.34. Its N-nitroso derivative formed minute prisms from dilute acetone, m.p. 272–275.5°. Calcd. for $C_{31}H_{36}N_2O_{11}$: C, 60.77; H, 5.92; OCH_3, 15.20. Found: C, 60.78; H, 5.91; OCH_3, 15.18. V was also obtained by treatment of IV with methanolic HCl, m.p. 179–185°. Found: C, 63.41; H, 6.44. Acetylation of either IV or V gave mixtures from which identical N-acetyl derivatives (VI) were isolated. VI contained an additional O-acetyl group. VI obtained from IV had m.p. 274–279°, $[\alpha]^{29}\mathrm{D}$ +9.4° (c 0.32 in chf.). Calcd. for $C_{35}H_{41}NO_{12}$: C, 62.96; H, 6.19. Found: C, 63.42; H, 6.26. VI obtained from V had m.p. 272–277°, $[\alpha]^{29}\mathrm{D}$ +9.7° (c 0.31 in chf.). Found: C, 63.07; H, 6.24. A mixture of the two derivatives showed no m.p. depression.

The origin and nature of the neutral nitronitroso derivative,[6] $C_{31}H_{35}N_3O_{13}$, obtained by the action of nitric acid on oxonitine and oxoaconitine can now be interpreted more readily. It apparently is formed from oxoaconitine by the loss of a mole of methanol, by replacement of the N-acetyl group with a nitroso group and by the introduction of a nitro group. In the case of oxonitine, a preliminary oxidation of CHOH to C=O must occur. The details of these transformations will be presented more fully at a later date.

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[6] W. A. Jacobs and L. C. Craig, *J. Biol. Chem.*, **136**, 323 (1940).

THE INFLUENCE OF HYDROGEN AND CARBON MONOXIDE PARTIAL PRESSURES ON THE RATE OF THE HYDROFORMYLATION REACTION

Sir:

Previous work[1] in this laboratory on the kinetics of the hydroformylation reaction showed that the rate was proportional to the concentration of olefin and approximately proportional to the concentration of dicobalt octacarbonyl catalyst, while it was essentially independent of the pressure of synthesis gas (H_2:CO, 1–2) in the range of 120 to 380 atm. Since the reaction is thermodynamically possible at low pressures of synthesis gas,[2] we have now studied the hydroformylation reaction at low partial pressures of hydrogen and carbon monoxide.

Contrary to the prevailing opinion that increased pressure facilitates the hydroformylation reaction, our new semi-quantitative data secured with cyclohexene at 110 and 115° under widely differing H_2:CO partial pressures show the following surprising results: (1) At constant carbon monoxide pressures the rate greatly increases with increasing hydrogen pressure. (2) At constant hydrogen partial pressures, the rate increases with increasing partial pressures of carbon monoxide up to about 10 atm. but decreases with higher partial pressure of carbon monoxide.

It is thus apparent that our previous observation on the independence of rate with pressure was owing to the relatively equal but opposite effects of increasing the partial pressure of the two gases, hydrogen and carbon monoxide.

Experimental.—A solution of cyclohexene and dicobalt octacarbonyl (34 g. and 1.4 g. per 100 g. of solution, respectively) in toluene was treated at 110 ± 1° for 68 minutes in a series of experiments under 10 atm. of CO and at various partial pressures of H_2. When the partial pressure of H_2 was 27, 54 and 110 atm., the conversion of olefin to cyclohexanecarboxaldehyde was 30, 51, and 65%, respectively.

With 55 atm. of H_2 and under otherwise identical conditions except that the partial pressure of CO was 3, 5, 14, 28 and 54 atm., olefin conversions of 35, 46, 43, 29 and 18%, respectively, were secured.

With a constant H_2:CO ratio of unity and total pressures of 53, 110 and 220 atm., the conversion of olefin was 15.3, 18 and 17.3%, respectively, again illustrating the apparent independence of rate at relatively high pressure of 1:1 gas.

When 2-ethyl-1-hexene was employed, essentially the same results as above were secured.

Discussion.—The above data may be explained if, in the initial stage of the reaction, some equilib-

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[1] G. Natta and R. Ecoli, *Chimica e Industria*, **34**, 503 (1952).

[2] G. Natta, P. Pino and E. Mantica, *ibid.*, **32**, 201 (1950).

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

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

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

$$[Co(CO)_3]_4 + 4CO \rightleftharpoons 2[Co(CO)_4]_2 \quad (3)$$

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.

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

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RECEIVED MAY 3, 1954

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.

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RECEIVED JULY 8, 1954

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-

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[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).