(18 min.) formed when 5 mole% Br_2 undergoing the Br^{80m}(4.4 hr.) $\xrightarrow{\text{I.T.}}$ Br^{80} (18 min.) reaction was dissolved in n-C_3H_7Br.

For the (n,γ) activation experiments highly purified n-C_3H_7Br containing 5 mole% Br_2 was irradiated in the Argonne National Laboratory CP5 reactor for 30 min. at 10^{12} neutrons cm.$^{-2}$ sec.$^{-1}$ and subsequently extracted with aqueous sulfite. The total "organic yield"[1] was 24%. Fifty microliters was placed on the gas chromatography column. Nitrogen flowed through at 40 ml./min. The column consisted of 6 ft. of 4 mm. i.d. glass tubing, bent in a U. The most satisfactory packing tried was crushed Johns-Manville C-22 insulating brick, sieved to 40–60 mesh, washed with water, dried and coated with 40% of its weight of General Electric SF-96(40) silicone oil. During a 30-min. separation run, the temperature of the oil-bath in which the column was immersed was raised from 60 to 200°, which allowed components of successively higher boiling point to move through the column at a desirable rate. The effluent gas passed to the bottom of a thin-walled 1-ml. glass thimble which fit in the well of a NaI(Tl) scintillation crystal. The scintillation crystal fed through a photomultiplier tube, preamplifier, linear amplifier and rate meter to a chart recorder. The first peak of each chromatogram in Fig. 1 was caused by about 10^5 dis./min., *i.e.*, about 10^{-13} g. of CH_3Br^{82}(36 hr.) or 10^{-15} g. of CH_3Br^{80}(18 min.).

With 6-ft. columns packed with insulating brick, the pressure required to maintain a 40 ml./min. flow rose from 3 lb. gage at 60° to 6 lb. at 200°. With Celite 545 packing, the required pressure rose to over 30 lb. after several runs. The two packings gave equally good resolution. Overlapping peaks were more completely resolved in the same time by use of a 12-ft. column of C-22 brick with a 60 ml./min. flow maintained by a 12 to 19 lb. pressure. Di-(2-ethylhexyl) phthalate ("Octoil") coatings gave resolution which was inferior to the silicone oil and also showed signs of decomposition at the higher temperatures.

Previous investigations[2,3] of the organic products of the Br^{81}(n,γ)Br^{82} process in n-C_3H_7Br containing 5 mole% Br_2, made by fractional distillation with added carriers, have identified ten compounds with the following relative percentages[3]: CH_3Br (5.8%), C_2H_5Br (1.4%), i-C_3H_7Br (3.4%), n-C_3H_7Br (35.7%), CH_2Br_2 (4.6%), $C_2H_4Br_2$ (6.5%), 1,2-$C_3H_6Br_2$ (10.5%), n-$C_6H_{13}Br$ (1.4%), 1,3-$C_3H_6Br_2$ (10.4%), 1,1,2-$C_2H_3Br_3$ (4.4%), higher boiling (15.7%). Many of these can be correlated with peak heights of Fig. 1. Definite assignment of all the peaks should be possible by calibration with known compounds, using a thermal conductivity detector.

Curves A and B of Fig. 1 are consistent with the conclusion that the product distributions from activation by the (n,γ) and isomeric transition processes are identical,[4,5] although they do not exclude small quantitative differences.

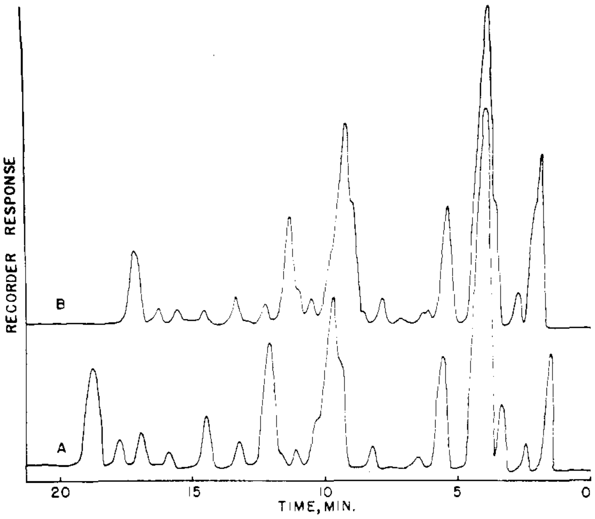

Fig. 1.—Gas chromatogram of trace compounds in n-C_3H_7Cr obtained with 6-ft. Celite 545-silicone oil column: Curve A, activated by (n, γ) process, monitored with scintillation counter; curve B, activated by isomeric transition, monitored with Geiger tube. Curves are not corrected for radioactive decay. The shorter retention time in Curve B was caused by a slightly faster heating rate.

Among the places where the techniques reported here should be valuable is in the separation of radioactive products formed by the photolysis or radiolysis of radioactive compounds or compounds containing dissolved radioactive halogens to scavenge free radicals.

This work was supported in part by the Atomic Energy Commission and by the University Research Committee.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN
JAMES B. EVANS
JOHN E. WILLARD

RECEIVED APRIL 27, 1956

---

(2) M. S. Fox and W. F. Libby, *J. Chem. Phys.*, **20**, 487 (1952).

(3) J. C. W. Chien, Ph.D. Thesis, University of Wisconsin, 1954.

(4) J. F. Hornig and J. E. Willard, THIS JOURNAL, **75**, 461 (1953).

(5) G. Levey and J. E. Willard, *ibid.*, in press (1956).

TERNARY OXIDES OF TETRAVALENT MOLYBDENUM

Sir:

We have prepared ternary oxides of tetravalent molybdenum containing divalent magnesium, zinc, cobalt and iron which are of an apparently new structural type. The general formula is $A_4Mo_6O_{16}$ ($A = Mg^{+2}, Zn^{+2}, Co^{+2}, Fe^{+2}$). We have also prepared a ternary oxide with calcium having the composition $CaMoO_3$.

Recently, Scholder and Brixner[1,2] reported the preparation of several ternary oxides of molybdenum, among them $CaMoO_3$ and $MgMoO_3$. However no chemical analyses or X-ray data were given for these compounds. Our results are in agreement with their findings for $CaMoO_3$ but in contrast to their work we have been unable to prepare a compound of composition $MgMoO_3$. All attempts to prepare this compound led to the formation of $Mg_4Mo_6O_{16}$.

All preparations were made by heating appropriate mixtures of the constituents in evacuated, sealed, silica capsules for 48 hours at 1150°. The

---

(1) R. Scholder, *Angew. Chem.*, **66**, 467 (1954).

(2) R. Scholder and L. Brixner, *Z. Naturforschg.*, **10b**, 178 (1955).

composition of the mixture was decided by the equations

$$4AO + 6MoO_2 \longrightarrow A_4Mo_6O_{16} \quad (A = Mg^{++}, Zn^{++}, Co^{++}) \qquad (1)$$

$$6Fe_2O_3 + 8Mo + 10MoO_3 \longrightarrow 3Fe_4Mo_6O_{16} \qquad (2)$$

$$CaO + MoO_2 \longrightarrow CaMoO_3 \qquad (3)$$

The use of a 50% excess of AO in reaction (1) did not affect the composition of the ternary oxide formed.

Chemical analysis of the calcium compound gave the following results. *Anal.* Calcd for $CaMoO_3$: Ca, 21.78; Mo, 52.14. Found: Ca, 21.54; Mo, 52.34. The X-ray powder diffraction pattern of this material can be indexed on the basis of a monoclinic unit cell with $a = c = 7.80 \pm 0.01$ Å., $b = 7.77 \pm 0.01$ Å. and $\beta = 91° 23' \pm 6'$. The observed density of 5.20 ± 0.05 g./cc. is in good agreement with the value of 5.17 g./cc. calculated for a unit cell containing 8 molecules of $CaMoO_3$. This compound apparently has a distorted perovskite structure similar to that of $YCrO_3$.[3]

The magnesium and zinc compounds can be obtained pure by washing the products of the solid phase reaction in dilute hydrochloric acid. The X-ray powder patterns of these compounds indicate that they are isomorphous with each other. The patterns can be indexed on the basis of a hexagonal unit cell with $a = 5.775 \pm 0.005$ Å. and $c = 9.915 \pm 0.010$ Å. for the zinc compound and $a = 5.761 \pm 0.005$ Å. and $c = 9.893 \pm 0.010$ Å. for the magnesium compound. The powder patterns of the cobalt and iron compounds are identical in nature to those of the magnesium and zinc compounds. Chemical analysis of the zinc compound coupled with density measurements and unit cell data for both the magnesium and zinc compounds clearly indicate that the general formula is $A_4Mo_6O_{16}$.

Anal. Calcd. for $Zn_4Mo_6O_{16}$: Zn, 23.92; Mo, 52.66. Found: Zn, 23.99; Mo, 52.89. Density: Calcd. for $Mg_4Mo_6O_{16}$: 5.43 g./cc. Found: 5.30 ± 0.06 g./cc. Calcd. for $Zn_4Mo_6O_{16}$: 6.33 g./cc. Found: 6.23 ± 0.06 g./cc.

Single crystals of the magnesium and zinc compounds have been grown which are suitable for X-ray analysis and structure determination is now in progress. Work is also being carried out in an attempt to extend this structure to other A and B cations.

This work has been supported by a contract between the Office of Naval Research and the University of Connecticut. Reproduction in whole or part is permitted for any purpose of the United States Government.

[3] L. Katz, *Acta Cryst.*, **8**, 121 (1955).

CHEMICAL LABORATORIES
UNIVERSITY OF CONNECTICUT
STORRS, CONNECTICUT

WILLIAM H. MCCARROLL
ROLAND WARD
LEWIS KATZ

RECEIVED MAY 4, 1956

A SIMPLE, RAPID METHOD FOR DETERMINATION OF METAL CHELATE STABILITY CONSTANTS

Sir:

A mercury electrode can be used as an indicator electrode for any metal ion in the presence of a chelating agent which forms a 1:1 complex with mercury(II) as well as with the metal ion in question. The potential is given by

$$E = E^{\circ}_{Hg^{++}} + \frac{RT}{2F} \ln \frac{[Me^{+\nu}][HgZ^{2-n}]K_{MeZ}}{[MeZ^{\nu-n}][K_{HgZ}} \qquad (1)$$

So, in a solution, containing a metal ion, $Me^{+\nu}$, and constant concentrations of its chelate complex, $MeZ^{\nu-n}$, as well as of the mercury chelate complex, HgZ^{2-n}, the potential of a mercury electrode depends only on the $Me^{+\nu}$-ion concentration. However, pure logarithmic dependence is only warranted if the stability constant of the metal complex, $MeZ^{\nu-n}$, is several orders of magnitude smaller than that of the mercury complex, HgZ^{2-n}. On the other hand, *for various metal ions this potential depends linearly on the logarithm of the stability constant of the complex,* K_{MeZ}, and is, within a certain *p*H region, independent of *p*H. The stability constants, K_{MeZ}, therefore can be calculated by equation (1) using the observed potential of the mercury electrode, the concentrations occurring in (1) and the stability constant K_{HgZ}.[1]

The stability constant K_{HgZ} can be determined in a similar way. The potential of a mercury electrode in a solution containing mercury(II) chelate complex and excess chelating agent is

$$E = E^{\circ}_{Hg^{++}} + \frac{RT}{2F} \ln \frac{[HgZ^{2-n}]\phi}{[Z^{-n}]K_{HgZ}} \qquad (2)$$

where

$$\phi = 1 + \frac{[H^+]}{K_n} + \frac{[H^+]^2}{K_nK_{n-1}} + \cdots + \frac{[H^+]^n}{\overset{n}{\underset{j=1}{\pi}} K_j}$$

K_j are the acidity constants of the complexing agent.

Equation (2) involves ϕ and hence the potential is *p*H dependent. In a solution containing equal amounts of mercury complex and free complexing agent, one simply measures the potential as a function of *p*H and calculates the stability constant, K_{HgZ}, from equation 2.

For a test of the method, the stability of the complexes of ethylenediaminetetraacetic acid (EDTA or Y) with several metal ions have been determined (Table I) and were found in excellent agreement with values obtained by other methods.

Potentials were measured as a function of *p*H, in solutions containing metal ion $Me^{+\nu}$, metal complex MeY^{--}, and mercury complex HgY^{--}, each 0.001 *M*, with the ionic strength kept at 0.1 by means of sodium perchlorate. For these definite concentrations, the potentials corresponding to various stability constants were calculated by means of equation (1) and plotted on a potential–*p*H diagram. The stability constants for a particular metal ion can then be directly read from the potential independent region of the experimental points.

In the case of the more stable complexes (Pb, Cu, Ni), the measurements were disturbed by the formation of white precipitates of mercurous mercury-

---

[1] G. Schwarzenbach, R. Gut, G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954), G. Schwarzenbach, G. Anderegg, *ibid.*, **37**, 1289 (1954), have mentioned briefly the applicability of mercury electrodes for the determination of metal chelate stability constants although neither the principle of the method nor details of operation were described.