activity coefficients

$$\frac{\bar{m}_6}{\bar{m}_7} \times \frac{m_7}{m_6} = 1 + \epsilon = \left(\frac{\bar{\gamma}_7}{\bar{\gamma}_6} \times \frac{\gamma_6}{\gamma_7}\right) \qquad (1)$$

where the bar marks the stronger solution. Equation 1 takes account of the fact that the solutions are mixtures of two electrolytes, utilizing Brφnsted's rule. The ratio of the activity coefficients in the dilute solution equals about unity. Hence

$$\ln (1 + \epsilon) \simeq \epsilon \simeq (\ln \bar{\gamma}_7 - \ln \bar{\gamma}_6) \qquad (2)$$

Glueckauf[2] has shown that the hydration parameters which largely determine the trends of the activity coefficients are a function of the Pauling radius of the cation. Equally—without making use of the hydration concept—the activity coefficients of the aqueous solutions of alkali salts of the same halogen can be directly expressed as functions of the Pauling radii (r, in ångström). The activity coefficients of all alkali chlorides at 25° for $m > 1$ are adequately expressed by the equation[3]

$$\ln \gamma = 0.60\sqrt[3]{\bar{m}} + km \qquad (3)$$

where

$$k = 0.270\,((1/r) - 0.38) \qquad (4)$$

The differences of the Pauling radii for Li^6 and Li^7 are known from Thewlis' measurement[4] of the lattice constants of Li^6F and Li^7F. These data give

$$(r)_{Li^6} - (r)_{Li^7} = 0.0004 \pm 0.00007 \text{ ångström} \qquad (5)$$

From equations 2, 3, 4, 5 follows

$$\epsilon = \left(\frac{\partial \ln \gamma}{\partial r}\right)_m \times \Delta r = \frac{0.270\,\bar{m}}{(r_{Li})^2} \times (r_6 - r_7) = 3 \times 10^{-4}\bar{m} \qquad (6)$$

where $r_{Li} = 0.60$ Å.

TABLE I

% DVB	Approx. exchanger molality ($\bar{m}$)	$10^3\ \epsilon$ observed (ref. 1)	$10^3\ \epsilon$ calculated for LiCl solutions ($\bar{m}$) from eqn. 6
4	3	1.0	0.9
8	5.5	1.6	1.7
12	7.5	2.7	2.3
16	9	3.7	2.7
24	12.5	3.8	3.8

Table I shows the agreement between the separation factors ϵ observed,[1] when the isotopes were separated on various exchanger types of different crosslinking (divinyl benzene content) by elution with dilute hydrochloric acid solution, and those calculated for the equilibria between a dilute and a concentrated lithium chloride solution of the same molal concentration as the exchanger.

Equation 6 can be used also for the reverse process of calculating the differences in ionic radius from observed isotopic separation factors, *e.g.*, for the case of the isotopes Na^{22} and Na^{24}.[5] On Dowex 50 ($\bar{m} \sim 6$) this gave $\epsilon = 1.4 \times 10^{-4}$ at 25°. Hence from eq. 6

$$r_{22} - r_{24} = \frac{\epsilon (r_{Na})^2}{0.270\bar{m}} = \frac{1.4 \times 10^{-4} \times 0.95^2}{0.27 \times 6} \simeq 8 \times 10^{-5} \text{ ångström}$$

The radii of two adjoining Na-isotopes would thus differ by only a tenth of the difference between the Li-isotopes, this being the square of the inverse ratio of the masses. If this principle applies generally, the outlook for enriching isotopes of higher mass by pure ion exchange is very dim indeed. One would expect for the exchange on Dowex 50

$$K^{39}\text{–}K^{41} \quad \Delta r = 2 \times 10^{-5}\text{Å. and } \epsilon = 1.8 \times 10^{-5}$$

and for

$$Rb^{85}\text{–}Rb^{87} \quad \Delta r = 5 \times 10^{-6}\text{Å. and } \epsilon = 3.5 \times 10^{-6}$$

ATOMIC ENERGY RESEARCH ESTABLISHMENT
HARWELL, ENGLAND E. GLUECKAUF

RECEIVED JULY 13, 1959

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π-CYCLOPENTADIENYL-π-CYCLOHEPTATRIENYL VANADIUM

Sir:

The chemical literature contains several examples of the preparation of cyclopentadienyl-metal carbonyl compounds by heating together a metal carbonyl and cyclopentadiene or dicyclopentadiene.[1] However, when molybdenum hexacarbonyl or iron pentacarbonyl is heated with cycloheptatriene, there is no loss of hydrogen to form tropylium compounds. Instead the complexes $C_7H_8Mo(CO)_3$[2] and $C_7H_8Fe(CO)_2$[3] are produced. The only tropylium sandwich compound so far reported is the ionic compound $[C_7H_7Mo(CO)_3]BF_4$, prepared by a different method.[4]

Using a different approach to tropylium-sandwich chemistry, the reaction between cyclopentadienyl vanadium tetracarbonyl[5] and cycloheptatriene was investigated. A mixture of $C_5H_5V(CO)_4$ (0.01 mole) and 30 ml. of commercial cycloheptatriene was refluxed under nitrogen at 120° for 9 hours. After removal of excess cycloheptatriene a black residue remained. Sublimation at 80° yielded oily material which was discarded. Further sublimation at 100° afforded 0.82 g. (yield 40%) of purple crystals, $C_5H_5VC_7H_7$, sparingly soluble in organic solvents to give purple solutions which in air begin to deposit a brown precipitate after a few minutes.

Anal. Calcd. for $C_{12}H_{12}V$: C, 69.6; H, 5.8; V, 24.6; mol. wt., 207. Found: C, 69.7, 69.8; H, 5.8, 5.8; V, 24.6; mol. wt., 229 (cryoscopic in benzene).

The analytical results are in less accord with a composition $C_5H_5VC_7H_8$ (C, 69.2; H, 6.25) than for $C_5H_5VC_7H_7$. However, a clearer demonstration of the nature of the new vanadium compound is provided by its magnetic properties. It is paramagnetic with $\lambda^{298°}_{\text{mole}} = 1055 \times 10^{-6}$ cm.^{3}-mole^{-1}, corresponding to 1.69 B.M., which is equivalent to one unpaired electron. This confirms the composition as $C_5H_5VC_7H_7$ rather than

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(1) For a recent review of compounds wherein an aromatic ring system and carbon monoxide groups are simultaneously bonded to metal atoms, see E. O. Fischer and H. P. Fritz, "Advances in Inorganic and Radiochemistry" (Eds. H. J. Emeléus and A. G. Sharpe) **1**, 55 (1959), Academic Press, Inc., New York, N. Y.

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$C_5H_5VC_7H_8$, since the latter would be a cycloheptatriene derivative of vanadium$^{\mathrm{I}}$ with two unpaired electrons. The vanadium compound should most probably be formulated as $C_7H_7^+V^0C_5H_5^-$(I). However, in the solid state it is stable in air at room temperature, only beginning to decompose at about 130°, in distinct contrast to the isoelectronic $(C_6H_6)_2V$.[6] Perhaps it is possible to explain the increased stability of $C_5H_5VC_7H_7$ over $(C_6H_6)_2V$ by regarding the former as a resonance hybrid of I and $C_7H_7^-V^{\mathrm{II}}C_5H_5^-$(II). Although the cycloheptatriene anion, isoelectronic with a "planar" cycloöctatetraene molecule with eight π-electrons, is not normally stable, the existence of $C_8H_8Fe(CO)_3$ and $C_8H_8[Fe(CO)_3]_2$[7] indicates that stable sandwich compounds can be formed by 8 π-electron systems, suggesting that the canonical form (II) might have some importance.[8]

We thank the Milton Fund for support of this work, the Shell Chemical Corporation for a gift of cycloheptatriene, and Union Carbide Metals Company for a gift of vanadium halides.

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(8) Because of the possibility of occurrence of this type of resonance designation of the π-C_7H_7 group in $C_5H_5VC_7H_7$ as "cycloheptatrienyl" rather than "tropylium" seems preferable. According to conventions now in use it is also difficult, or even perhaps unwise, to assign a definite oxidation state to the vanadium.

(9) National Science Foundation predoctoral fellow 1958–1960.

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ISOLATION OF 5-METHOXYINDOLE-3-ACETIC ACID FROM BOVINE PINEAL GLANDS[1]

Sir:

During the isolation and characterization of melatonin,[2] a substituted 5-hydroxyindole derivative in the pineal gland that can lighten pigment cells, we found a chemically related but biologically inactive compound. The latter, now identified as 5-methoxyindole-3-acetic acid (I), is the first demonstration of O-methylation of a 5-hydroxyindole. This compound had not been known to exist in biologic tissue although it had been isolated as a urinary excretion product in rats after administration of 5-methoxytryptamine.[3]

One hundred grams of trimmed lyophilized bovine pineal glands[4] was powdered in a blender and defatted with petroleum ether in a soxhlet extracter. The powder was mixed with 1700 ml. water in a blender for two minutes and the mixture centrifuged at 16,000 × *g* for 30 minutes. The supernate was passed through glass wool and extracted twice with equal volumes of ethyl acetate. The ethyl acetate layers were taken to dryness *in vacuo*. The residue was subjected to countercurrent distribution of 29 transfers with the upper phase moving in a system of ethyl acetate:heptane:water in a 1:1:2 ratio. Tubes 7 to 22 were combined and taken to dryness *in vacuo*. The residue was dissolved in benzene and put on a silicic acid column. With 0.75% methanol in benzene, I was eluted, evaporated to dryness, and the residue rerun through the countercurrent distribution and the silicic acid column. The final product was sublimed at 75° for three hours *in vacuo* to give 400 μg. of I.

Ultraviolet light absorption maximum of I was at 2760 Å. with shoulders at 2960 and 3080 Å. No appreciable acid–base shift of the maximum occurred. Maximum fluorescence was at 338 mμ and maximum activation at 304 mμ. Infrared examination showed a broad carbonyl absorption at 1710 cm.$^{-1}$ and the possible presence of a methoxyl group. A strong blue violet color was obtained with Ehrlich reagent. Electrophoretic studies showed that the compound migrated as if it had a free carboxyl group.

Ultraviolet absorption and fluorescence properties and the reaction with Ehrlich reagent indicated that the compound was a 5-hydroxyindole derivative. The lack of a significant acid–base shift of the ultraviolet absorption maximum signified that the hydroxy group was blocked. The Ehrlich reaction indicated that positions 1 and 2 probably were free. Ultraviolet and infrared data showed that the carboxyl, detected by electrophoretic studies, was not conjugated with the ring.

Because extremely small amounts of material were available, final evidence for the structure of I was obtained by mass spectrometry. The methyl ester, prepared by treating I with diazomethane, had a mass of 219. A strong peak at mass 160 indicated the structure of a fragment as CH_3O–C_8H_5N–CH_2–. These data suggested that the structure for I was 5-methoxyindole-3-acetic acid. I was synthesized from 5-methoxyindole-3-acetonitrile.[5,6,7] The synthetic and natural compounds were found to have identical chemical and physical properties as determined by reaction with Ehrlich reagent; infrared, ultraviolet absorption and fluorescence curves; countercurrent distribution; silicic acid column; and paper chromatography with acidic, basic and neutral solvents. Mass spectrometry of the methyl esters of both synthetic and natural I revealed the same proportion of 219 and 160 masses.

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