ATP itself. Thus it showed a single ultraviolet–visible spot on ascending paper chromatography in both an acidic solvent system[10] (R_f 0.44) and in a basic solvent system[11] (R_f 0.32) and a single spot on polyethylenimine cellulose thin layer chromatography using 0.5 *N* LiCl as the eluent (R_f 0.39).[7] The spots could also be visualized using the periodate–benzidine spray of Viscontini, *et al.*,[12] which is diagnostic for the presence of the *vic*-dihydroxyl group in the ribose ring.

The proton nmr spectrum taken at 100 MHz was consistent with the assigned structure. The spectrum (D_2O) showed δ 2.25 (2 H, apparent triplet, $J_{P-H} = 20$ Hz), 2.33 (2 H, apparent triplet, $J_{P-H} = 20$ Hz), 4.20 (5 H, multiplet), 6.25 (1 H, doublet, $J_{H-H} = 6$ Hz), 8.28 (1 H, singlet), 8.44 (1 H, singlet). Upon decoupling of the phosphorus (irradiation at 40.5 MHz; NMR Specialties heteronuclear decoupler) the pair of apparent triplets centered at δ 2.29 collapsed to a single broad peak, with a width at half-height of 18 Hz. Moreover, a broad peak which constituted the major component of the multiplet centered at δ 4.20 also partially collapsed. This peak, presumably arising from the methylene hydrogens on the 5′ carbon of the ribose moiety, changed from having a width at half-height of 12 Hz to having a width at half-height of 6 Hz.

Unlike either ATP or its known α,β- and β,γ-monomethylene analogs,[13–15] the bismethylene analog, which contains no labile P–O–P linkages, is stable to strongly acidic aqueous solutions for long periods of time. The stability of the ester linkage in the bismethylene analog is similar to that of a monoester of a phosphonic acid.[16] Investigations into the potential inhibitory properties and use as a substrate analog in enzymatic systems requiring ATP (*e.g.*, S-adenosylmethionine synthetase) are in progress.

Acknowledgments. This work was supported in part by the U. S. Public Health Service, Grant AM 13529. We wish to thank Mr. Richard Neese for his help with the phosphorus decoupling experiment.

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Received December 31, 1969

Preparation of Potassium Trihydridomagnesiate, $KMgH_3$

Sir:

The importance of complex metal hydrides of aluminum and boron (*e.g.*, $LiAlH_4$ and $NaBH_4$) in both organic and inorganic chemistry is well known.[1] Complex metal hydrides of alkali metals with magnesium, although highly sought after, are unknown. For example, in an attempt to prepare $LiMgH_3$, Tanaka[2] reported that hydrogenolysis of a mixture of methyllithium and dimethylmagnesium at elevated temperatures formed a mixture of LiH and MgH_2. Coates[3] recently reported that pyrolysis of the *n*-butyllithium adduct of dimethylmagnesium (presumably $LiMg(CH_3)_2C_4H_9$) formed a mixture of LiH and dimethylmagnesium.

We wish to report the first successful synthesis of a complex metal hydride of an alkali metal and magnesium. The compound $KMgH_3$ (potassium trihydridomagnesiate) was prepared by the hydrogenolysis of $KMg(sec\text{-}C_4H_9)_2H$ in benzene solution.[4] The solubility

$$KMg(sec\text{-}C_4H_9)_2H \xrightarrow{H_2} KMgH_3 + 2C_4H_{10} \qquad (1)$$

of $KMg(sec\text{-}C_4H_9)_2H$ in benzene is unique and avoids the necessity of hydrogenolysis in more basic solvents, such as ethers, thus eliminating the competition between solvent and hydride ion for coordination sites in the expected product. In addition, secondary butyl groups bonded to relatively electropositive metals are known to undergo hydrogenolysis under relatively mild conditions. This factor allows reduction of this compound at room temperature where it is known to exist as an authentic $KMgR_2H$ complex. This is an important point since high-temperature hydrogenation of Lewis acid–base complexes of this type might be preceded by extensive dissociation at the higher temperatures, followed by reduction, forming a mixture of alkali metal hydride and magnesium hydride, according to

$$KMgR_2H \rightleftharpoons KH + MgR_2 \xrightarrow{H_2} KH + MgH_2 + 2RH \qquad (2)$$

Hydrogenolysis of a 0.5 *M* benzene solution of potassium di-*sec*-butylhydridomagnesiate (K:Mg:butyl:H = 1.0:1.0:1.9:0.95) under 3000 psi of hydrogen pressure at 25° for 4 hr resulted in quantitative precipitation of a yellow solid which reacted violently when exposed to the atmosphere. This solid was analyzed for alkali metal (by flame photometry), magnesium (by EDTA titration), and hydrogen (by gas evolution analysis). Analysis gave a potassium, magnesium, and hydrogen ratio of 1.0:1.0:3.0. *Anal.* Calcd for $KMgH_3$: K, 58.7; Mg, 36.8; H, 4.52. Found: K, 58.9; Mg, 36.2; H, 4.56. No butane was produced on hydrolysis, indicating complete reduction and formation of a $KH:MgH_2$ species. These analytical data are also consistent with the formation of a physical mixture of KH and MgH_2. However, X-ray powder analysis (Table I) revealed a unique diffraction pattern, different from the patterns for KH and MgH_2, indicating that the reaction product is not a physical mixture. The strongest line for KH (at 3.30 Å) and strongest lines for MgH_2 (at 3.19, 2.495, 1.67, and 1.59 Å) are clearly absent from the $KMgH_3$ pattern. Preliminary studies on $KMgH_3$ indicate that it is insoluble in common hydrocarbon and ether solvents, stable to disproportionation, and

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Table I. X-Ray Pattern Data[a]

KH	MgH_2	$KMgH_3$	$KMgF_3$[5]
3.30 (vs)	3.19 (vs)	4.003 (vw)	
2.86 (s)	2.76 (vw)	3.137 (vvw)	
2.02 (s)	2.495 (vs)	2.835 (vs)	2.80 (m)
1.72 (s)	2.29 (m)	2.311 (m)	2.29 (m)
1.43 (m)	1.59 (s)	2.007 (s)	1.99 (vs)
1.65 (m)	1.67 (s)	1.794 (vw)	
1.31 (m)	1.50 (m)	1.639 (s)	1.625 (m)
1.28 (m)	1.42 (w)	1.420 (m)	1.408 (m)
1.17 (m)	1.36 (w)	1.268 (m)	1.259 (w)
1.10 (m)	1.335 (w)	1.184 (m)	1.201 (s)
1.01 (w)	1.246 (w)	1.158 (w)	1.150 (w)
	1.150 (w)	1.122 (vw)	
	1.125 (w)		

[a] X-Ray powder diffraction data were obtained using a Philips Norelco X-ray unit, using an 11.46-cm diameter camera with Ni-filtered Cu Kα radiation. Line intensities were estimated visually.

does not cleave ether solvents. A preliminary study of the thermal properties of $KMgH_3$ as determined by simultaneous dta–tga analysis revealed a weak, broad, exothermic effect at ~250°, which may indicate disproportionation to KH and MgH_2, followed by endothermic effects at 300 and 380° due to decomposition of MgH_2 and KH, respectively. $KMgH_3$ was also prepared by a pyrolytic olefin elimination reaction when KMg(*sec*-C_4H_9)$_2$H was heated in light mineral oil at 80° under vacuum.

$$\mathrm{KMg}(sec\text{-}\mathrm{C_4H_9})_2\mathrm{H} \xrightarrow{\Delta} \mathrm{KMgH_3} + 2\mathrm{C_4H_8} \qquad (3)$$

Comparison of the powder pattern data for $KMgH_3$ with that of $KMgF_3$ suggests that these two compounds are isomorphous, a result predicted from the similar ionic radii of F^- and H^-. The Perovskite-like structure was demonstrated for $KMgF_3$[5] and is thus implied for $KMgH_3$. This structure is found for ABX_3 systems (A = B = metal cations, X = anion) in which one cation is much larger than the other. It is described as a cubic close-packed arrangement of the anions and the larger cations, with the smaller cations occupying octahedral positions in an ordered pattern.[6] It is proposed that each magnesium cation of $KMgH_3$ is surrounded by an octahedral arrangement of hydride ions. The crystal structure of MgH_2 was clearly shown[7] to be that of rutile, which also involves an octahedral array of hydride ions about each magnesium cation. The environment about magnesium in $KMgH_3$ and MgH_2 is therefore predicted to be essentially equivalent. Independent verification of this prediction is obtained from comparison of the infrared spectra (obtained as a Nujol mull between KBr salt plates) for these two compounds. MgH_2 exhibits two broad absorption envelopes centered at 1160 and 650 cm^{-1}. These are assigned to metal–hydrogen stretching and deformation vibrations, respectively. The infrared spectrum of $KMgH_3$ revealed two similarly broad absorptions centered at 1150 and 680 cm^{-1}. The absence of pronounced shifts is verification of nearly equivalent environments in these compounds.

We are currently investigating other routes to $KMgH_3$ and the preparation of related tri- and tetrahydridomagnesiate compounds. Detailed studies designed to describe the chemical and physical properties of these compounds are being carried out.

Acknowledgment. We are indebted to the Office of Naval Research under Contract No. NOOO 14-67-A-0159-0005 and ONR Contact Authority No. NR-93-050/12-5-67-429 for support of this work.

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Received January 8, 1970

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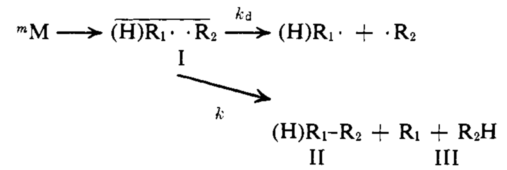
Theory of Chemically Induced Nuclear Spin Polarization. III.[1] Effect of Isotropic *g* Shifts in the Components of Radical Pairs with One Hyperfine Interaction[2]

Sir:

In two recent communications we have shown how hyperfine-coupling-induced singlet–triplet mixing in radical pairs can lead to large nuclear polarizations in products derived from radical coupling and disproportionation reactions.[1] Independently, Kaptein and Oosterhoff proposed a very similar mechanism and made the connection between nuclear and electron spin polarizations.[3,4] However, this model covers only part of the experimental observations and is restricted to radical pairs with at least two different protons coupled to the electrons in the radical pair. The polarization of the product is of the type in which the total nuclear Zeeman energy of the molecules is not changed from equilibrium (integral over entire spectrum = 0) and was termed entropy polarization.[5] In this communication, we wish to extend the theory and show that inclusion of spin–orbit coupling in the model can explain energy polarization in products (integral over polarized spectrum $\lessgtr 0$).

As a model, we consider a weakly coupled radical pair (I) generated from a precursor ^{m}M in a single step, where *m* denotes the multiplicity of M. A finite fraction of the radical pairs is assumed to react inside the solvent cage to give the combination or disproportionation products of II or III, with the remainder diffusing apart to give free radicals. For simplicity, it is assumed



$$^m\mathrm{M} \longrightarrow \overline{\underset{\mathrm{I}}{(\mathrm{H})\mathrm{R}_1\cdot\ \cdot\mathrm{R}_2}} \xrightarrow{k_d} (\mathrm{H})\mathrm{R}_1\cdot + \cdot\mathrm{R}_2 \qquad (1)$$

$$\xrightarrow[k]{} \underset{\mathrm{II}}{(\mathrm{H})\mathrm{R}_1\text{–}\mathrm{R}_2} + \underset{\mathrm{III}}{\mathrm{R}_1 + \mathrm{R}_2\mathrm{H}}$$

that only one of the two components of I, [(H)$R_1\cdot$], has a proton spin strongly coupled to the electron spin

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[1] I and II of this series are: G. L. Closs, *J. Amer. Chem. Soc.*, **91**, 4552 (1969); G. L. Closs and A. D. Trifunac, *ibid.*, **91**, 4554 (1969).

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