The Preparation and Characterization of Potassiumtriisobutyldialuminum and Tripotassiumdecaisobutylpentaaluminum

EUGENE P. SCHRAM

Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210, U.S.A.

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Abstract

The reaction between $Al_2{}^iBu_4$ and K results in the formation of K^iBu and $KAl_2{}^iBu_3$. The latter reacts with additional K to produce $K_3Al_5{}^iBu_{10}$. The oxidation states of aluminum, associated with these reduced aluminum compounds, have been determined by oxidative hydrolyses. Spectroscopic characterization included infrared and NMR data; ^1H, ^{13}C, ^{27}Al, and ^{39}K.

Introduction

The potassium reduction of $^iBu_2AlCl$ has been described affording the catenated aluminum compound, $Al_2{}^iBu_4$ (I) [1]. The chemical reactivity of I with several protonic and hydritic reagents [2], and Lewis bases [3] has likewise been reported. In a related manner, Al^iBu_3 has been treated with K to afford $K_2Al_2{}^iBu_6$ and the latter described as containing Al^{2+}, *i.e.* an Al–Al bond [4]. More recently Al^iBu_2H has been reported to react with K to produce analogous $K_2Al_2Bu_4H_2$ (II) also described as containing Al^{2+} [5]. Concerning the latter reaction, when excess K is employed, decomposition takes place accompanied by the formation of $[KAl^iBu_3H]_2$, KBu, KH and Al(O) [6]. We now report the reaction between $Al_2{}^iBu_4$ (III) and K which initially produces $KAl_2{}^iBu_3$ followed by further reaction of the latter with additional K to afford $K\ Al^iBu_4$, K^iBu, Al(O) and $K_3Al_5{}^iBu_{10}$.

Results and Discussion

The reaction products of $Al_2{}^iBu_4$ (I) with K are typically red–brown oils and are extremely difficult to separate. Characterization included oxidative hydrolysis to afford ½ mol H_2 per mol Al^{2+}, in the absence of the Al–H moiety. Throughout this investigation we have not observed aluminum hydride formation. This conclusion was reached based on the absence of Al–H in the ^1H NMR spectrum, *ca.* 3 ppm [6], the absence of ν(Al–H), typical and non-typical [6] in the infrared spectrum, and absence of formation of HD upon treatment of reaction products with DCl. Concerning the latter reaction, the AlH moiety affords HD whereas Al^{2+} produces D_2.

With regard to the reaction system studied, I was dissolved in cyclopentane and allowed to react with K. After the reaction period, excess K, K^iBu, and Al(0) were separated from the soluble components by filtration, *in vacuo*. After investigation of the soluble components (utilizing an aliquot of the reaction products), the K reduction was continued. This procedure resulted in the analytical characterization of four different cyclopentane soluble reaction mixtures which were produced in sequence.

The employed investigative methods involved obtaining NMR (^1H, ^{13}C, ^{27}Al, ^{39}K) and infrared data on the soluble reaction mixtures, as well as carrying out acid hydrolyses. The latter allowed calculation of average Al oxidation states because H_2 is evolved during hydrolysis of compounds containing Al in oxidation states less than 3+. For all reaction mixtures, two components adequately described the product mixture because exact characterization was not the goal but rather trends in the average Al oxidation state.

Reaction of $Al_2{}^iBu_4$ with K

The initial reaction between I and K is ideally described by eqn. (1).

$$Al_2{}^iBu_4 + 2K \longrightarrow KAl_2{}^iBu_3 + K^iBu \qquad (1)$$

In addition to $KAl_2{}^iBu_3$ (II), $Al_2{}^iBu_4$ is present (13% molar) based on analytical characterization. It has not been possible to isolate pure II because both I and II have similar solubility characteristics, are nonvolatile prior to decomposition, and both react with additional K. Furthermore, the reactivity of these species has precluded chromatographic separation. With regard to reaction of the last 13% of $Al_2{}^iBu_4$ with K, this system results in the reduction of I, but is accompanied by further reaction of II with K to afford KAl^iBu_4, K^iBu, Al(O) and $K_3Al_5{}^iBu_{10}$.

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TABLE I. Analytical Data Associated with the Reaction System $Al_2{}^iBu_4$ and K

Stoichiometry of material isolated	Aluminum Average oxidation state		Mole ratio										Equivalent weight (mg/mmol H_2)	
			$^iBu/H_2$		$^iBu/Al$		H_2/Al		Al/K		$^iBu/K$			
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc
$KAl_2{}^iBu_3 + 0.15\ Al_2{}^iBu_4$	1.2+	1.1+	1.6	1.7	1.4	1.6	0.89	0.89	2.48	2.3	3.6	3.6	140	142
$KAl_2{}^iBu_3 + 0.82KAl^iBu_4$	1.58+	1.58+	2.6	3.1	1.8	2.2	0.71	0.71					233	252
$KAl_2{}^iBu_3 + 2KAl^iBu_4$	2.0+	2.0+	5.4	5.5	2.8	2.8	0.54	0.50	1.2	1.3	3.4	3.7	425	426
$KAl_2{}^iBu_3 + 7.1KAl^iBu_4$	2.56+	2.56+	14.8	15.7	3.3	3.4	0.22	0.22	1.1	1.1	3.7	3.8	1123	1176
$K_3Al_5{}^iBu_{10}$	1.48+	1.40+	2.6	2.5	2.0	2.0	0.76	0.80	1.6	1.7	3.3	3.3	217	206

Characterization of Reaction Products

The initial reaction between **I** and K affords $KAl_2{}^iBu_3$ (**II**) as the principle product where $KAl_2{}^iBu_3$ represents the simplest formula. The composition of the soluble reaction components, $KAl_2{}^iBu_4$: $0.15Al_2{}^iBu_4$ is consistent with the analytical data summarized in Table I. Both the equivalent weight (mg/mmol H_2) and mmol H_2/mmol Al are in excellent agreement with the indicated mixture composition. These data confirm that further reduction of **I** has taken place. In addition, the calculated average Al oxidation state, 1.1^+ is very near the experimental value, 1.2^+.

The solution of composition $KAl_2{}^iBu_3 + 0.15Al_2{}^iBu_4$ was treated with additional K followed by filtration to afford the solution of composition $KAl_2{}^iBu_3 + 0.82KAl^iBu_4$. The two component nature of this system is most likely an over simplification based on the indicated calculated and observed ratios of $^iBuH/H_2$ etc., however, it is clear that the average Al oxidation state has increased from 1.2+ to 1.58+. In the same manner, this reaction mixture was treated with additional K to afford material of composition $KAl_2{}^iBu_3 + 2KAl^iBu_4$, Table I. Regarding the latter mixture, complete analytical characterization was effected with the calculated and experimental values in excellent agreement. Again, the average oxidation state of the cyclopentane soluble components has increased, 1.58+ to 2.0+. In a related manner, the equivalent weight (mg/mmol H_2) has increased from that initially found, 140, to 233, and now 425.

The final reaction carried out with K produced soluble material of composition $KAl_2{}^iBu_3$ + 7.1-KAl^iBu_4 which exhibited an average Al oxidation state of 2.56+ and an equivalent weight of 1123 (found), calc. 1176, Table I.

To summarize this series of reactions, $Al_2{}^iBu_4$ reacts with K to afford $KAl_2{}^iBu_3$ (**II**) and KBu. **II** reacts further with additional K to produce KAl^iBu_4, K^iBu and Al(O) with **II** and KAl^iBu_4 constituting the cyclopentane soluble products.

NMR data associated with $KAl_2{}^iBu_3$, $KAl_2{}^iBu_3 + 0.82KAlR_4$, and $KAl_2{}^iBu_3 + 7.1KAl^iBu_4$ are summarized in Table II along with the reported K derivatives, KAl^iBu_4 and $K_2Al_2{}^iBu_6$. In all cases of K derivatives, the $CH_2\delta$ is *ca.* −0.30 whereas for neutral species such as Al^iBu_3 and $Al_2{}^iBu_4$, δ is 0.24 and 0.32, respectively [6]. In the case of $KAl_2{}^iBu_3 + 0.82KAl^iBu_4$, overlapping doublets are present at *ca.* δ −0.29 whereas for the composition $KAl_2{}^iBu_3 + 7.1KAl^iBu_4$ a single doublet is observed at δ −0.30. An interesting feature of the ^{39}K NMR is δ −30, that is highly shielded K. We have previously reported shielded ^{39}K, δ −22, associated with $[KAl^iBu_3H]_2$, and have raised the possibility of K covalently bonded [6]. Regarding the present study, all reaction mixtures exhibited an ^{27}Al signal

TABLE II. NMR Parameters Associated with Isobutyl Organoaluminum Compounds

Compound	^{1}H (ppm) (J (Hz))			^{13}C (ppm) {^{1}H}			^{27}Al (ppm) ($W_{1/2}$ (Hz))	^{39}K ($W_{1/2}$ (Hz))
	CH(septet)	CH_3(d)	CH_2(d)	CH_3	CH	CH_2		
$KAl_2{}^iBu_3$[a]	2.14 (6.45)	1.29 (6.45)	−0.30 (6.70)	29.6[b]	28.4[b]	23.0[b]	147 (336)	−30 (980)
$KAl_2{}^iBu_3 + 0.82KAl^iBu_4$[c]		1.35 (6.60)	−0.29, −0.28 overlapping (d)	29.5[b]	28.3[b]		147 (355)	−33 (360)
$KAl_2{}^iBu_3 + 7.1KAl^iBu_4$[a]	2.14 overlapping septets	1.30 (6.5) overlapping (d)	−0.30 (6.9)	29.6[b] 29.2[b]	28.4[b]		147 (280) 10% 135 (373)	
$K_3Al_5{}^iBu_{10}$[a]	2.13 (6.4)	1.28 (6.35)	−0.31 (6.05)	29.7[b]	28.4[b]		147 (426)	−3vw (1000)
$K_3Al_5{}^iBu_{10}$[c,d]		1.37(s)	−0.34(s)				154 (1573)	
KAl^iBu_4[a,e]			−0.25					
$K_2Al_2{}^iBu_6$[a,e]		1.3	−0.30					

[a] Benzene-d_6. [b] Established by off resonance. [c] Toluene-toluene-d_8. [d] −50 °C. [e] Ref. 4.

of *ca.* δ 147. For the composition $KAl_2{}^iBu_3 + 7.1KAl^iBu_4$, a second ^{27}Al, δ 135, is observed at *ca.* 10% that of δ 147. In a related manner, this system exhibits two $^{13}C(CH_3)$ resonances at δ 29.6 and 29.2. In general K derivatives of Al-isobutyl compounds exhibit $^{13}C(CH_3)$ resonances δ 29.1–29.8 whereas for molecular species resonances are found at δ 28.0–28.3 [6]. Similarly, $^{13}C(CH)$ (K derivatives) resonances are found in the range δ 28.3–28.7 whereas for molecular compounds the range is δ 26.3–26.7.

Returning to the reaction between Al_2Bu_4 and K, in addition to the insoluble reaction products, K^iBu and Al(O), $K_3Al_5{}^iBu_{10}$ (**III**) is produced. **III** is insoluble in cyclopentane but very soluble in benzene, hence separation of **III** from K^iBu, K and Al(O) was effected by filtration *in vacuo.*

Characterization of $K_3Al_5{}^iBu_{10}$

Treatment of **III** with acid is described by eqn. (2) with the experimental quantities indicated in parentheses.

$$K_3Al_5{}^iBu_{10} + 8H^+ + 10H_2O \longrightarrow$$
$$3(3.07)K^+ + 5(5.0)Al(OH)_2{}^+ + 10(10.08){}^iBuH + 4(3.8)H_2 \qquad (2)$$

In order to investigate the possible alternate H_2 source, eqn. (2), (the Al–H moiety) rather than, or in addition to reduced oxidation state Al, **III** was treated with DCl. After correcting for the employed DCl/HCl composition of this reagent no HD was produced. Therefore **III** does not contain the Al–H moiety. Consistent with this conclusion is the fact that the IR spectrum of **III**, does not exhibit either typical ν(Al–H) (~1800br,s cm^{-1}) or non-typical ν(Al–H) (~1470br,s cm^{-1}) [6].

The indicated stoichiometry for **III** represents the simplest formula. A solution molecular weight measurement, in benzene, was unsuccessful based on the fact that equilibrium could not be obtained (isopiestic method). Mass spectral measurements were also unsuccessful.

NMR data associated with **III** are summarized in Table II. Equivalent ^{i}Bu moieties are indicated by the ^{1}H and ^{13}C data at room temperature and –50 °C. The ^{27}Al δ, 147, is the same as that observed for $KAl_2{}^iBu_3$, although the ^{39}K δ is –3 for **III**, as contrasted to –30 found for $KAl_2{}^iBu_3$.

A possible bonding model for **III**, assuming the indicated simplest formula is the molecular formula, consists of five catenated Al with two ^{i}Bu moities bonded to each Al as a 3– ion with 3K$^+$ associated as a tight ion pair (**III** is very soluble in benzene). The equivalence of the ^{i}Bu moieties may be the result of rapid exchange. This bonding model involves both three and four coordinate Al and therefore would be expected to exhibit two ^{27}Al NMR absorptions; only one was observed with a fairly narrow line width for ^{27}Al, 426 Hz. An alternate geometry involves a trigonal bipyramid of Al atoms; if one assumes Al SP^2 hybridization with ^{i}Bu moieties in the trigonal plane (equatorial ^{i}Bu), and ^{i}Bu groups in the yz planes (axial ^{i}Bu). This geometry results in the following group orbital irreducible representations: axial P_z, $A_1 + B_1$; axial SP^2, $A_1 + B_1$; equatorial P_x, $A_2 + 2B_1$; and equatorial SP^2 $2A_1 + B_2$. The following four molecular orbital combinations would be bonding: A_1 (SP^2) axial + A_1 (SP^2) equatorial; A_1 (SP^2) equatorial + A_1 (P_z) axial; B_1 (SP^2) axial + B_1 (P_x) equatorial; and B_1 (P_z) axial + B_1 (P_x) equatorial. This bonding model would account for the accomodation of 8 bonding electrons which is consistent with the formation of 4 mol H_2 per mol **III**.

With regard to the two suggested geometries for **III**, the catenated model involves three coordinate Al, therefore **III** may exhibit Lewis acid character. On the other hand excess negative charge is associated with Al, based on the ^{1}H δ CH_2, hence the Lewis acidity would be decreased. **III** was treated separately with NMe_3 and $HNMe_2$, and in both cases these reagents were quantitatively recovered indicating **III** does not function as an electrophile. Furthermore **III** does not evolve isobutylene in the temperature range 25–112 °C whereas both $Al_2{}^iBu_4$ and Al^iBu_3 exhibit this characteristic by 90 °C [3]. The geometry (bonding) associated with **III** results in increase thermal stability regarding isobutylene evolution, *i.e.* βH migration.

Summary

All of the reduced oxidation state Al compounds discussed are red–brown oils which have not been successfully crystallized to date possibly due to the unsymmetric nature of the ^{i}Bu moiety. The initial reaction of K with $Al_2{}^iBu_4$ involves elimination of K^iBu accompanied by formation of further reduced Al of stoichiometry $KAl_2{}^iBu_3$. Treatment of the latter with K is summarized by eqn. (3). Based on the analytical characterization of the cyclopentane

$$4K + 7KAl_2{}^iBu_3 \longrightarrow K_3Al_5{}^iBu_{10} + KAl^iBu4 + 7K^iBu + 8Al(0) \qquad (3)$$

soluble species, $KAl_2{}^iBu_3$ and KAl^iBu_4, the solutions examined represent 85%, 93% and 98% completion of the reaction described by eqn. (3). Current studies involve the preparation of analogous compounds replacing the ^{i}Bu moiety with neopental in an effort to obtain crystalline materials.

Experimental

Equipment and Techniques

Standard vacuum line procedures were employed throughout this investigation [7]. Filtrations were carried out *in vacuo* employing a medium porosity glass frit assembly equipped with O ring joints and teflon stop cocks. Infrared spectra were recorded with a Unicam SP 1100 spectrometer with a film of nonvolatile samples prepared by vaporization of the appropriate solvent in a N_2 atmosphere. Volatile materials were contained in a 10 cm gas cell, KBr optics. FT NMR spectra were obtained with a Bruker AM-500 Spectrometer employing benzene-d_6 or toluene-d_8. Nonvolatile samples were transferred to 10 mm NMR tubes in an inert atmosphere. Visible spectra were obtained using a Cary 170 spectrophotometer whereas ESR spectra were recorded using a Varian E-112 spectrometer. Solvents were distilled onto these materials, *in vacuo,* and the NMR tubes fuse sealed. ^{27}Al and ^{39}K spectra were referenced to aqueous 1 M $Al(NO_3)_3$ and 1 M KNO_3, respectively. Mass spectra, H_2, HD and D_2 were obtained with a Balzers QME 112 Quadrupole Spectrometer.

Analyses

Hydrolyses were carried out *in vacuo* with 20% HCl. Dihydrogen was collected in a volume calibrated Toepler pump assembly and identified by combustin to H_2O over CuO at 300 °C. Aluminum and potassium were determined gravimetrically after precipitation as the 8-hydroxyquinolate [8] and tetraphenyl borate [9], respectively. Standard solutions of both elements, employing similar dilutions as unknowns, yielded 99% plus recovery of the respective cations. Isobutane quantities were determined by employing the ideal gas law. Identification was confirmed by vapor tension measurements and infrared spectroscopy.

Reagents

Diisobutylaluminum chloride, from Ethyl Corporation, was used as received while quantities were measured volumetrically in a N_2 atmosphere. Solvents utilized, cyclopentane, benzene-d_6, and toluene-d_8 were dried *in vacuo* using n-BuLi after solvent removal from the latter *in vacuo.* Solvents were then purified by fractional condensations until their respective vapor tensions agreed with the literature values. Deuterium chloride, obtained from Cambridge Isotope Laboratories, 99% D, was used as received. Prior to reactions employing DCl, the necessary portion of the vacuum line was treated with DCl, P ~600 torr. Next, fresh DCl to be used as a reactant was expanded in the same portion of the vacuum line and an aliquot was examined by gas phase IR to determine the HCl–DCl composition by integration of the appropriate relative IR absorptions. Trimethylamine and dimethylamine were dried over P_2O_5 followed by fractional distillation *in vacuo* until their respective vapor pressures matched the literature values.

Preparation of $KAl_2{}^iBu_3$

$^iBu_2AlCl$, 8 ml (41 mmol) dissolved in 25 ml cyclopentane, was slowly added to 1.6 g K slivers, 41 mmol, and magnetically stirred in the presence of 25 ml cyclopentane. Reactants were maintained at 0 °C for 24 h followed by 48 h at *ca.* 25 °C. Cyclopentane, 25 ml, was added to the thick dark brown reaction mixture followed by an additional 1.6 g K, and this system was stirred for an additional 2 days at *ca.* 25 °C. Filtration of this red–brown reaction mixture, cyclopentane, afforded $KAl_2{}^iBu_3 + 0.15Al_2{}^iBu_4$. *Anal.* Calc.: Al, 20.46; K, 12.8; ^{i}Bu, 67.0. Found: Al, 21.7; K, 12.6; ^{i}Bu, 65.7. NMR data are summarized in Table II. The insoluble reaction residue was red–brown in color.

Reaction of $KAl_2{}^iBu_3$ with K

The material characterized as $KAl_2{}^iBu_3 + 0.15Al_2{}^iBu_4$, dissolved in cyclopentane, was stirred with *ca.* 1 g K for two days at *ca.* 25 °C followed by filtration to afford $KAl^iBu_4 + 0.82KAl^iBu_4$. This procedure was repeated producing $KAl_2{}^iBu_3 + 2KAl^iBu_4$. *Anal.* Calc.: Al, 12.7; K, 13.8; ^{i}Bu, 73.6. Found: Al, 12.4; K, 15.0; ^{i}Bu, 72.8. The reaction mixture of stoichiometry, $KAl_2{}^iBu_3 + 2KAl^iBu_4$ was again treated with *ca.* 1 g K to afford $KAl_2{}^iBu_3 + 7.1KAl^iBu_4$. *Anal.* Calc.: Al, 10.5; K, 13.6; ^{i}Bu, 75.9. Found: Al, 10.9; K, 14.1; ^{i}Bu, 75.1.

Isolation and Characterization of $K_3Al_5{}^iBu_{10}$ (III)

The repeated reaction of $KAl_2{}^iBu_3$ with K affords red–brown **III** which is insoluble in cyclopentane. **III** was separated from excess K, K^iBu and Al(0) by filtration *in vacuo* employing benzene. Acid hydrolysis of the colorless insoluble material produced ^{i}BuH and H_2. Acid hydrolysis of **III**, 150.2 mg, produced isobutane, 1.83 mmol and H_2, 0:69 mmol. *Anal.* Calc. for **III**: Al, 16.4; K, 14.3; ^{i}Bu, 69.3. Found; Al, 16.3; K, 14.5; ^{i}Bu, 69.4. Treatment of **III** with excess DCl (84%) produced 0.019 mmol H_2, 0207 mmol HD and 0.51 mmol D_2. Mmol Al–Al $= (0.51)/(0.84)^2 = 0.72$; mmol AlH = 0.02. NMR data associated with **III** are summarized in Table II. Principle infrared absorptions: 2945(s), 2855(s), 2755(s), 1465(m), 1372(m), 1358(m), 1315(m), 1164(s), 1038(s), 945(w), 811(s), 670(s) and 632(s) cm^{-1}. A diethyl ether solution of **III** exhibits a broad absorption from 400 to 665 nm centered at *ca.* 550 nm. A. benzene solution of **III** did not exhibit an ESR signal at 25 °C. A sample of **III** was heated in the mass spectrometer from 36 to 140 °C; no masses above ^{i}BuH were observed.

Reactivity of III

A sample of **III**, 145.2 mg, was slowly heated *in vacuo* to 112 °C; no H_2 or ^{i}BuH were produced. **III**, 150 mg, dissolved in benzene, was treated with NMe_3, 6.10 mmol, ($P \sim 700$ torr) for 2 h at *ca.* 25 °C. NMe_3 was quantitatively recovered. Next **III** was treated with $HNMe_2$, 6.55 mmol, under the same reaction conditions; $HNMe_2$ was quantitatively recovered. An isopiestic molecular weight determination was attempted in benzene. The apparatus allowed periodic determination of the standard and unknown (**III**) solution vapor pressures. Equilibrium was not established after one month. Although material precipitated from the unknown solution, the vapor pressure of the known solution was always greater than that of the solution of **III**. Apparently precipitation was accompanied by the formation of soluble decomposition products.

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References

1 H. Hoberg and S. Krause, *Angew. Chem., 88,* 760 (1976).
2 M. A. Miller and E. P. Schram, *Organometallics, 4,* 1362 (1985).
3 E. P. Schram and M. A. Miller, *Inorg. Chim. Acta, 113,* 131 (1986).
4 H. Hoberg and S. Krause, *Angew. Chem., 90,* 1013 (1978).
5 V. V. Gavrilenko and L. A. Chekulaeva, *Zh. Obshch. Khim., 53,* 481 (1983).
6 E. P. Schram, *Inorg. Chim. Acta, 134,* 117 (1987).
7 D. F. Shriver, 'The Manipulation of Air-Sensitive Compounds', McGraw-Hill, New York, 1969.
8 I. M. Kolthoff, E. G. Sandell, E. J. Meehan and S. Bruckenstein, 'Quantitative Chemical Analysis', 4th edn., MacMillian, New York, 1971, p. 600.
9 W. Geilmann and W. Gebauhr, *Z. Anal. Chem., 139,* 161 (1953).