E.S.R. Spectra and Reactivity of Alane Radical Anions in Solution

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Summary The structures and reactions of $H_3Al\bullet^-$ and $(Bu^tO)_3Al\bullet^-$, generated by abstraction of hydrogen from H_4Al^- and $(Bu^tO)_3AlH^-$, respectively, have been investigated in solution using e.s.r. spectroscopy.

ALTHOUGH lithium aluminium hydride is widely employed for the reduction of a variety of organic compounds, relatively little is known about the mechanisms of these reactions. The hydridoaluminates are usually considered to transfer nucleophilic hydrogen heterolytically to the substrate, but recent results suggest the involvement of free radicals in the reductions of certain organic halides, ketones, and polynuclear arenes by simple and complex metal hydrides.[1,2]

Consideration of possible radical chain mechanisms, with propagation steps shown in equations (1) and (2) (substitution) or (3) and (4) (addition), for reduction by hydridoaluminates, led us to examine the generation and reactivity of alane radical anions ($X_3Al\bullet^-$) in solution using e.s.r. spectroscopy.

$$X_3Al\bullet^- + Y\text{-}Z \rightarrow X_3\bar{Al}Y + Z\bullet \quad (1)$$

$$Z\bullet + H\bar{Al}X_3 \rightarrow ZH + X_3Al\bullet^- \quad (2)$$

$$X_3Al\bullet^- + Y{=}Z \rightarrow X_3\bar{Al}Y\text{-}Z\bullet \quad (3)$$

$$X_3\bar{Al}Y\text{-}Z\bullet + H\bar{Al}X_3 \rightarrow X_3\bar{Al}Y\text{-}ZH + X_3Al\bullet^- \quad (4)$$

U.v. photolysis of a tetrahydrofuran (THF) solution containing di-t-butyl peroxide (15% v/v) and tetra-n-butylammonium tetrahydroaluminate (*ca.* 0·3 M) at 180—295 K gave rise to an e.s.r. spectrum (see Figure) which we assign to the alane radical anion, $H_3Al\bullet^-$, formed by abstraction of hydrogen from H_4Al^- [equations (5) and (6)].[3]†

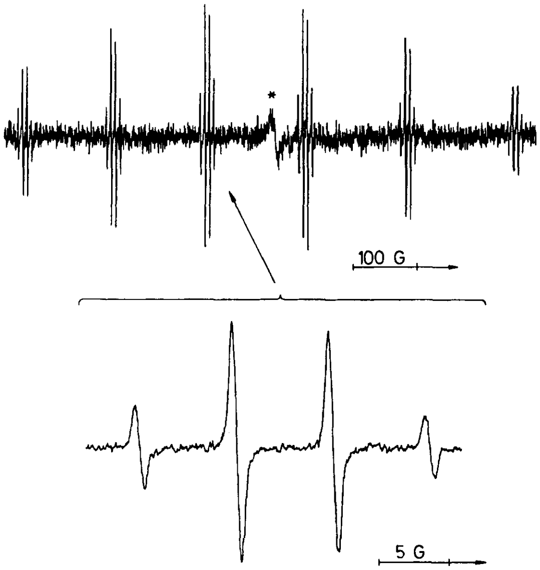

FIGURE. E.s.r. spectrum of $H_3Al\bullet^-$ obtained during continuous photolysis of a THF solution containing Bu^tOOBu^t and $Bu^n{}_4NAlH_4$ at 235 K. The broad peak marked with an asterisk is a permanent background signal from the spectrometer cavity.

TABLE. E.s.r. parameters for alane radical anions.

Radical	T/K	g-Factor[a]	Hyperfine splittings/G $a(^{27}Al)$[a]	 a(H or D)
$H_3Al\bullet^-$	230	2·0025	(+) 154·2[b]	7·0 (3H)[b]
$D_3Al\bullet^-$	230	2·0025	(+) 152·2[c]	1·05 (3D)[c]
$(Bu^tO)_3Al\bullet^-$	230	2·0015	(+) 300·7[d]	—
$H_3Si\bullet$[e]	203	2·0032	(−) 182[f]	(+) 7·84 (3H)[g]

[a] Calculated from resonance fields and microwave frequencies by exact solution of the isotropic Hamiltonian using the program ESRLSQ written by Dr. K. F. Preston (D. Griller and K. F. Preston, *J. Am. Chem. Soc.*, 1979, **101**, 1975). [b] $d|a(Al)|/dT$ − 28, $d|a(3H)|/dT$ − 4 mG K^{-1} for the radical derived from $Bu^n{}_4NAlH_4$. [c] $d|a(Al)|/dT$ − 28, $d|a(3D)|/dT$ − 0·6 mG K^{-1} for the radical derived from $Bu^n{}_4NAlD_4$. [d] $d|a(Al)|/dT$ + 87 mG K^{-1}. [e] From S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson, and K. D. J. Root, *J. Chem. Soc. A*, 1970, 348. [f] ^{29}Si Splitting from ref. 6. [g] Positive sign based on *ab initio* molecular orbital calculations (ref. 7).

$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO\bullet \quad (5)$$

$$Bu^tO\bullet + H_4Al^- \rightarrow H_3Al\bullet^- + Bu^tOH \quad (6)$$

A similar e.s.r. spectrum was obtained in THF when the tetrabutylammonium salt was replaced by $LiAlH_4$, although with the lithium counter-ion only the $M_I(^{27}Al)$ −1/2 quartet was well resolved.‡ However, in the presence of 12-crown-4 (which is known to complex Li^+ strongly) the spectrum was very similar to that obtained from the tetrabutylammonium salt. The trideuterioalane radical anion was generated similarly from $Bu^n{}_4NAlD_4$.

The tri-t-butoxyalane radical anion was produced in an analogous way by the abstraction of hydrogen from $Li(Bu^tO)_3AlH$ [equation (7)] in diglyme–dimethyl ether (1 : 1 v/v) and the e.s.r. parameters of this and the other alane radical anions are given in the Table.

$$Bu^tO\bullet + (Bu^tO)_3\bar{Al}H \rightarrow (Bu^tO)_3Al\bullet^- + Bu^tOH \quad (7)$$

The ^{27}Al splitting constant reported here for $H_3Al\bullet^-$ does not agree with that (223 G at 77 K) derived from a spectrum, detected previously in the solid state after γ-irradiation of $LiAlH_4$ or $NaAlH_4$, also assigned to this radical anion.[4]

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† The natural abundance of ^{27}Al (I 5/2) is 100%.

‡ This differential linewidth effect is probably related to ion association phenomena.

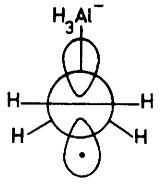
Comparison of our value with that calculated for unit population of the Al-3s orbital (985 G)[5] shows that the semi-occupied orbital in $H_3Al\cdot^-$ has *ca.* 16% Al-3s character. The corresponding Si-3s population in the isoelectronic silyl radical $H_3Si\cdot$ is 15% (see Table),[6] indicating a similar deviation from planarity for both radicals.[7] The magnitudes of a(3H) are also similar for both radicals, although the signs have not been determined experimentally.

The ^{27}Al splitting for $(Bu^tO)_3Al\cdot^-$ is appreciably larger than that for $H_3Al\cdot^-$ and corresponds to an Al-3s population of *ca.* 31%. Replacement of H by the more electronegative Bu^tO-group, which also has non-bonding electrons on oxygen,[8a] would be expected to induce increased deviation from planarity at Al.[8] The value of $a(^{27}Al)$ derived from a spectrum attributed[9] to $Me_3Al\cdot^-$ in the solid state (324 G) is surprisingly close to our value for $(Bu^tO)_3Al\cdot^-$ and it is clearly important to obtain isotropic spectra of alane radical anions with a variety of ligands in order to investigate substituent effects on structure.

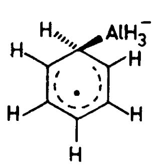
We are now undertaking a detailed study of the reactions of alane radical anions in solution and some preliminary results are given here. Photolysis at 205 K of a THF solution containing Bu^tOOBu^t, $Bu^n{}_4NAlH_4$, and a propyl halide afforded the e.s.r. spectrum of the propyl radical rather than that of $H_3Al\cdot^-$, implying that reaction (8; X = Cl, Br, or I) proceeds rapidly at low temperatures.§ Similar reactivity was shown by $(Bu^tO)_3Al\cdot^-$.

$$H_3Al\cdot^- + Pr^nX \rightarrow H_3\overset{-}{Al}X + Pr^n\cdot \qquad (8)$$

E.s.r. experiments have also shown that $H_3Al\cdot^-$ adds readily to ethylene to give a β-substituted ethyl radical [$a(2H_\alpha)$ 17·0,¶ $a(2H_\beta)$ 15·6,¶ $a(^{27}Al)$ 50·7, a(3H) 2·8 G; g 2·0026 at 208 K]. The hyperfine splitting constants indicate that the most stable conformation of the adduct is the 'eclipsed' structure (**1**), although there could be significant distortion from this idealised structure and the aluminium atom could be displaced toward the bridging position. Addition to benzene affords the cyclohexadienyl radical (**2**) [a(1H) 29·4, $a(^{27}Al)$ 53·7, a(3H) 1·6, $a(2H_o)$ 6·3, $a(2H_m)$ 1·4, $a(1H_p)$ 10·9 G; g 2·0027 at 253 K]. Deuterium-labelled analogues were generated to confirm the analyses of the e.s.r. spectra.



(1)



(2)

The alane radical anion thus resembles $H_3B\cdot^-$ and $H_3Si\cdot$ in its properties.[3]

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§ These reactions may be better regarded as electron-transfer processes rather than halogen-atom abstractions.

¶ Tentatively assigned on the basis of their temperature dependences; $d|a(2H_\alpha)|/dT$ *ca.* 0, $d|a(2H_\beta)|/dT = +5$ mG K^{-1}. The ^{27}Al splitting was essentially independent of temperature.

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