An E.S.R. Study of the Gallane Radical Anion

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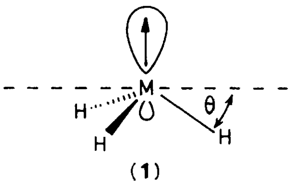
The isotropic e.s.r. spectrum of $H_3Ga^{\cdot-}$ has been observed, both in fluid solution and in the solid state, and the gallium hyperfine splitting indicates that the out-of-plane angle is similar to that for $H_3Al^{\cdot-}$.

The radicals $H_3X^{\cdot-}$, $H_3Y^{\cdot}$, and $H_3Z^{\cdot+}$ are isoelectronic when X, Y, and Z are elements of groups 3, 4, and 5, respectively, in the same row of the Periodic Table. The borane radical anion (**1**; M = B^-) is planar ($\theta_{min} = 0°$),† like the methyl radical and the ammonia cation radical,[1,2] although the input of energy required for out-of-plane bending probably increases appreciably along the series $H_3B^{\cdot-} < H_3C^{\cdot} < H_3N^{\cdot+}$.[3] In contrast, the alane radical anion (**1**; M = Al^-) is pyramidal and the isotropic ^{27}Al hyperfine splitting corresponds to *ca.* 16% unpaired electron population of the Al-3s orbital,[4] very similar to the analogous Si-3s population in $H_3Si^{\cdot}$ (see Table 1).[5] Hence it appears that $H_3Al^{\cdot-}$ and $H_3Si^{\cdot}$ have similarly pyramidal structures and *ab initio* molecular orbital calculations for the latter give $\theta_{min} = 17.6°$.[6] However, simple theory[1,7] predicts that θ_{min} should increase as M becomes increasingly less electronegative than H, and thus θ_{min} might be expected to increase across the series $H_3P^{\cdot+} < H_3Si^{\cdot} < H_3Al^{\cdot-}$.[1] It was thus of interest to generate the gallane radical anion $H_3Ga^{\cdot-}$ and we report here its e.s.r. spectrum in both rigid matrix and in solution and describe its chemical reactions with alkyl halides.



(**1**)

$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO^{\cdot} \qquad (1)$$

$$Bu^tO^{\cdot} + H_4Ga^- \longrightarrow H_3Ga^{\cdot-} + Bu^tOH \qquad (2)$$

The e.s.r. spectrum shown in Figure 1(a) was recorded at 212 K after γ-irradiation of polycrystalline tetra-n-butylammonium tetrahydrogallate[8] (TBAG) at 77 K. The spectrum is isotropic, apart from residual differential line broadening, and the sharpest line $[m_I(^{69}Ga) + \frac{1}{2}]$‡ appears as a poorly-resolved quartet under optimum instrumental conditions. Less intense, but better resolved, spectra of $H_3Ga^{\cdot-}$ were obtained during continuous u.v. irradiation of tetrahydrofuran (THF) or $[^2H_8]$THF solutions containing TBAG (*ca.* 0.4 M) and di-t-butyl peroxide (15% v/v) [equations (1) and (2)]. The $m_I(^{69}Ga)$ −3/2 quartet is shown in Figure 1(b) and the e.s.r. parameters for the gallane radical anion in $[^2H_8]$THF at 222 K are $a(^{69}Ga)$ 420.2, $a(^{71}Ga)$ 534.1, a(3H) 10.0 G, g 2.0055 (1 G = 10^{-4} T).§ The parameters derived from the solid state spectrum, $a(^{69}Ga)$ 421.1 and $a(^{71}Ga)$ 534.4 G at 182 K, are remarkably similar and imply that the umbrella angle of $H_3Ga^{\cdot-}$ is rather insensitive to the nature of the environment. The same is true of $H_3Al^{\cdot-}$, for which we find $a(^{27}Al)$ 154.8 G, g 2.0027 at 158 K when the radical is generated by γ-irradiation of polycrystalline $Bu^n{}_4NAlH_4$ at 77 K. For $D_3Al^{\cdot-}$ under similar conditions $a(^{27}Al)$ is 152.9 G, and thus for both isotopic species the aluminium splittings are equal within experimental error to those (154.2 and 152.2 G, respectively) obtained for the radicals in THF solution at 230 K.[4]

The value of a(Ga) for $H_3Ga^{\cdot-}$ does not vary significantly ($\not> \pm 0.8$ G) with temperature between 118 and 234 K, suggesting that only the ground vibrational state of the umbrella mode is populated to an appreciable extent in the temperature range investigated. The gallium hyperfine splitting corresponds[1] to 15.8% population of the Ga-4s orbital and, assuming orbital following, this implies that θ_{min} is very similar for $H_3Ga^{\cdot-}$ and $H_3Al^{\cdot-}$. The electronegativity of gallium is actually greater than that of aluminium (see Table 1) and clearly θ_{min} for (**1**) is not a very sensitive function of $(\chi_M - \chi_H)$ alone. The structures of $H_3Ga^{\cdot-}$ and the isoelectronic $H_3Ge^{\cdot}$ are evidently also similar.

In addition to electronegativity effects,[7] a number of more subtle factors presumably govern the value of θ_{min} for (**1**) and

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† It is important to distinguish between θ_{min} and θ_{av}. The former is the out-of-plane angle corresponding to the minimum potential energy, whilst the latter is the value of this angle averaged over the populated vibrational states.

‡ The natural abundances of ^{69}Ga and ^{71}Ga are 60.2 and 39.8%, respectively; I is 3/2 for both isotopes and $(\gamma^{69}Ga/\gamma^{71}Ga)$ is 0.787.

§ Calculated using Preston's program ESRLSQ (D. Griller and K. F. Preston, *J. Am. Chem. Soc.*, 1979, **101**, 1975).

Table 1

Radical	T/K	g-Factor	a(M)[a]/ G	a(3H)/ G	% Unpaired electron population of M-ns orbital[b]	χ_M[c]	Ref.
$H_3B^{\cdot-}$	253	2.0023	19.9 (11)	15.2	2.8 (2)	2.04	[d]
$H_3Al^{\cdot-}$	230	2.0025	154.2 (27)	7.0	15.7 (3)	1.61	[e]
$H_3Ga^{\cdot-}$	222	2.0055	420.2 (69)	10.0	15.8 (4)	1.81	This work
$H_3C^{\cdot}$	96	2.0026	38.3 (13)	23.0	3.4 (2)	2.55	[f]
$H_3Si^{\cdot}$	203	2.0032	182[g] (29)	7.8	15.0 (3)	1.90	[h]
$H_3Ge^{\cdot}$	4	2.012	75[i] (73)	15	14.1 (4)	2.01	[j]

[a] Mass number of isotope shown in parentheses. [b] Value of n shown in parentheses; splittings corresponding to 100% population taken from ref. 1. [c] Pauling scale; $\chi_H = 2.2$. [d] Ref. 2. [e] Ref. 4. [f] R. W. Fessenden, *J. Phys. Chem.*, 1967, **71**, 74. [g] For $Me_3Si^{\cdot}$ at 153 K, $a(^{29}Si)$ is 181.1 G; P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1969, **91**, 3938. [h] Ref. 5 and S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson, and K. D. J. Root, *J. Chem. Soc. A*, 1970, 348. [i] For $Me_3Ge^{\cdot}$ at 233 K, $a(^{73}Ge)$ is 84.7 G; R. V. Lloyd and M. T. Rogers, *J. Am. Chem. Soc.*, 1973, **95**, 2459. [j] G. S. Jackel, J. J. Christiansen, and W. Gordy, *J. Chem. Phys.*, 1967, **47**, 4274; R. L. Morehouse, J. J. Christiansen, and W. Gordy, *ibid.*, 1966, **45**, 1751.

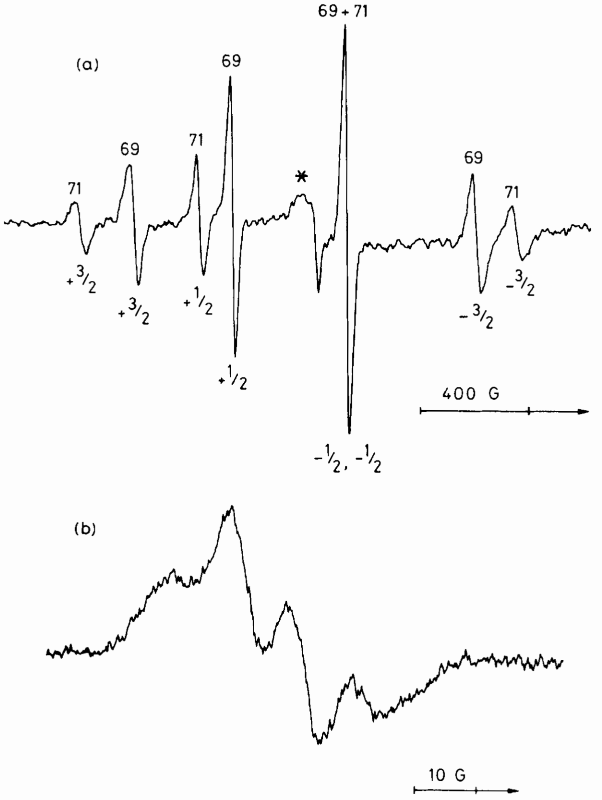

Figure 1. E.s.r. spectra of the gallane radical anion. (a) In polycrystalline $Bu^n{}_4NGaH_4$ at 212 K. The assignments to $H_3{}^{69}Ga^{\cdot-}$ and $H_3{}^{71}Ga^{\cdot-}$ and the magnetic quantum numbers are shown: the central absorption marked with an asterisk is not due to $H_3Ga^{\cdot-}$. The microwave frequency was 9125.30 MHz. (b) Expansion of the m_I $-3/2$ transition for $H_3{}^{69}Ga^{\cdot-}$ in [$^2H_8$]THF at 222 K showing the splitting from three equivalent protons.

we suggest that electrostatic repulsion between the hydrogen ligands may play an important role. In particular, $H_3Al^{\cdot-}$ has been predicted[1] to be more pyramidal than $H_3Si^{\cdot}$ on account of the orbital hybridisation differences[7] which result because aluminium is more electropositive than silicon. However, in addition to these through-bond effects there will be a repulsive coulombic interaction between the hydrogen ligands which acts through space. Because the electronegativity of aluminium is considerably less than that of hydrogen, most of the negative charge in $H_3Al^{\cdot-}$ will reside on the ligands and electrostatic repulsion between these will act to widen the HMH angle, that is to *reduce* θ_{min}. Electrostatic repulsion between the hydrogen atoms in $H_3Si^{\cdot}$ will be much smaller, because silicon is less electropositive than aluminium and the silyl radical is uncharged. We conclude that the response of θ_{min} to variations in (χ_M–χ_H), which is predicted[7] on the basis of consideration of hybridisation changes alone, will be offset by the concomitant changes in the electrostatic interactions between the ligands.

The gallane radical anion rapidly abstracts halogen from alkyl halides; $H_3Al^{\cdot-}$ and $H_3B^{\cdot-}$ are known to react similarly.[2,4] Thus, photolysis of [$^2H_8$]THF solutions containing TBAG, di-t-butyl peroxide, and Pr^{n}Cl, Bu^{t}Cl, or Pr^{n}Br (each halide *ca.* 1.3 M) at 200—230 K affords the spectrum of the corresponding alkyl radical and $H_3Ga^{\cdot-}$ is not detectable.

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