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Direct Observation of Aromatic Anion Radicals as Intermediates in the Reactions of Aromatic Compound Vapors with Calcium Atom

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Aromatic anion radicals as intermediates in the reactions of aromatic compound vapors with calcium atom were directly observed by ESR.

The study of metal vapor reactions has received considerable interest in organometallic chemistry and organic synthesis during recent years.[1)] This metal vapor procedure afforded both main group and transition metal compounds which can not be obtained by other methods or which were prepared only in low yields in solution. The direct observation of active intermediates is key problem to clarify the mechanism of metal vapor reactions. We previously reported the first activation of C-H bonds of aromatic ring by calcium atom followed by formation of arylcalcium hydrides.[2)] Aromatic anion radicals as reaction intermediates were also proposed. In this paper, we report the direct observation of aromatic anion radicals as intermediates in the insertion reactions of C-H bonds of aromatic ring with calcium atom by ESR. For this purpose, the apparatus for metal atom matrix ESR studies illustrated in Fig. 1 was made. The cryostat assembly attaches direct-

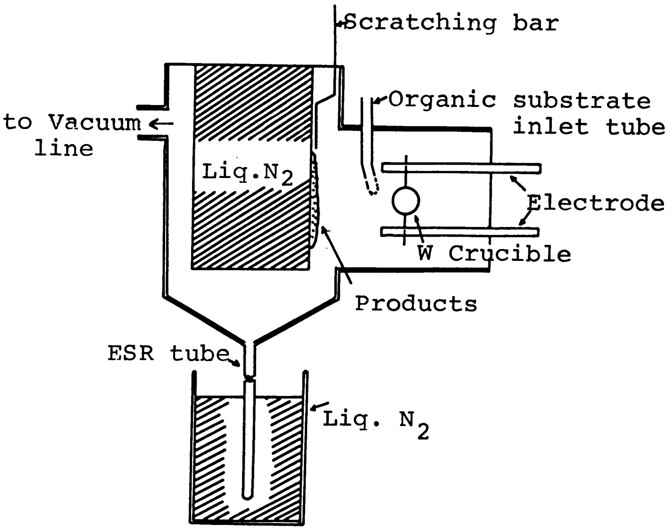
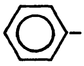
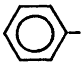


Fig. 1. The apparatus for metal atom matrix ESR studies.

Table 1. ESR Data for Products of Aromatic Compound Vapors-Calcium Atom

Compound	T/K	Hfs/mT (ring protons)	$g^{a)}$	Reference
	213	0.35	2.0027	this work
		0.376	2.0028	[3]
-Me	153	b)	2.0025	this work
		0.512(o-H), 0.544(m-H) 0.059(p-H)	2.0026	[3]
-Et	153	$0.5^{c)}$	2.0031	this work
		0.506(o,m-H), 0.092(p-H)	-	[3]
$-SiMe_3$	153	b)	2.0034	this work
		0.266(o-H), 0.106(m-H) 0.813(p-H)	-	[4]

a) The g factors were determined by reference to that of Fremy's salt (g= 2.0055). b) Not resolved. c) Hfs due to the para proton was not resolved.

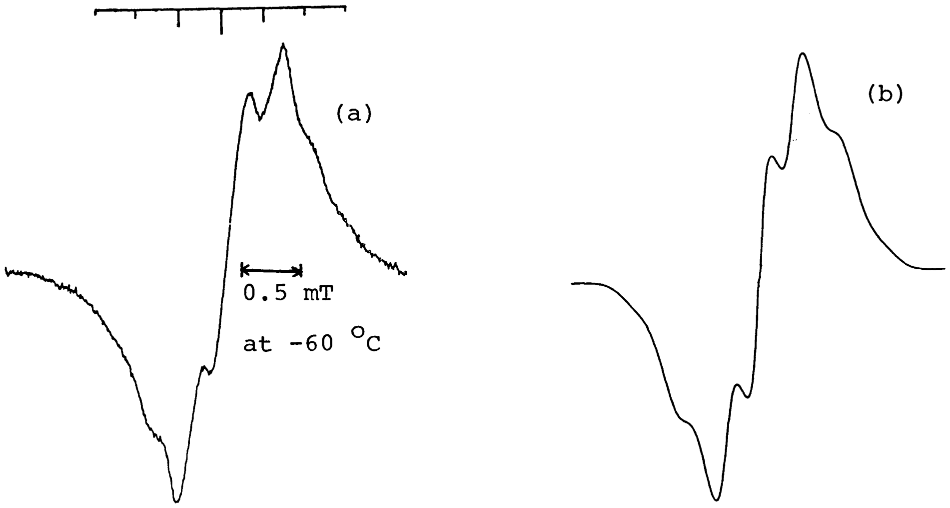


Fig. 2. (a) The observed ESR spectrum of benzene vapor-calcium atom product at -60 °C. (b) Computer simulated ESR spectrum using Lorentian line shape and a line width of 0.39 mT.

ly to the assembly for metal vaporization and is pumped out as part of the complete vacuum system. Direct measurements can be made of physical properties of active intermediates produced by the reactions of aromatic compound vapors with calcium atom by using this apparatus.5)

A typical experiment is as follows. Calcium metal (0.15 g, 3.7 mmol) was vaporized at a temperature of ca. 900 °C using a filament of tungsten in vacuo (ca. 5×10^{-3} Torr) at a rate of ca. 20 mg min^{-1}. During the vaporization of calcium metal, benzene (4 cm^3, 45 mmol) was introduced as vapor. Benzene vapor-calcium atom product condensed on the stainless-steel drum filled with liquid nitrogen. The product of benzene vapor-calcium atom at 77 K was transfered to the ESR tube by a scratching bar.

The ESR data of benzene, toluene, ethylbenzene, and phenyltrimethylsilane vapors-calcium atom, respectively, obtained by using this apparatus are summarized in Table 1. As a typical example, Fig. 2 shows the ESR spectrum of the product formed by the reaction of benzene vapor with calcium atom. Although the spectrum is poorly resolved, it consists of a septet and the linewidth is ca. 0.39 mT. The outermost lines of the septet are lost in the noise. The ESR spectrum of benzene vapor-calcium atom product can safely be assigned to the benzene anion radical by comparison with that of reference sample.3) The experimental spectrum was reproduced by computer simulation with the listed hyperfine splitting constants (hfs) shown in Table 1. The signal disappeared gradually on warming temperature at 0 °C. The product formed by the reaction of ethylbenzene vapor with calcium atom also afforded poorly resolved ESR spectrum with the linewidth of ca. 0.56 mT. The ESR spectrum of ethylbenzene vapor-calcium atom product is easily assigned to the ethylbenzene anion radical by comparison with the ESR data of reference sample3) and by computer simulation. The ESR spectra of the products formed by the reactions of toluene and phenyltrimethylsilane vapors with calcium atom, respectively, were found to be a broad siglet. The broad siglet may probably be resulted by the high concentrations of reaction intermediates. Although no hyperfine structures due to the ring protons were resolved, these signals may be attributed to the toluene and phenyltrimethylsilane anion radicals, respectively, from the ESR results of benzene and ethylbenzene vapors-calcium atom products and g factors.

These ESR results suggest that aromatic anion radicals are produced in the reactions of aromatic compound vapors with calcium atom.

In this work, we made a convenient apparatus for metal atom matrix ESR studies and observed directly aromatic anion radicals as intermediates in the reactions of aromatic compound vapors with calcium atom by ESR. This apparatus will give further information on reaction intermediates in metal vapor reactions.

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