ESR Studies of the Reaction of the Calcium Atom with Substituted Benzene Vapors[1]

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The reaction of the calcium atom with substituted benzene vapors was examined by means of ESR. The anion radicals of substituted benzenes as intermediates were directly observed.

The study of metal-vapor reactions has been of considerable interest in organometallic chemistry and organic synthesis during the last few decades.[2] With these methods, it is proving feasible to synthesize organometallic compounds which would be difficult, if not impossible, to prepare by other methods, and to study their reactive intermediates. The unstable intermediates (molecules and molecular fragments) produced by metal-vapor reactions are generally stabilized at cryogenetic temperatures in a solid matrix.

The unstable intermediates in metal-vapor reactions are mainly being examined by means of matrix infrared and Raman spectroscopy.[2] Matrix electron spin resonance (ESR) is also potentially useful in these studies. However, there have been few reports on a convenient apparatus for high-boiling metal matrix ESR.[3]

We previously reported the activation of the C–H bonds[4] and C–X bonds[5] of substituted benzenes by a calcium atom, followed by the formation of the corresponding arylcalcium hydrides and arylcalcium halides respectively. In these studies, the anion radicals of substituted benzenes were proposed to be reactive intermediates.

In this paper, we will describe the preparation of a convenient apparatus for high-boiling metal matrix ESR and also ESR studies of the reactions of the calcium atom with substituted benzene vapors using this apparatus.

Results and Discussion

In studying the activation of C–H bonds[4] and C–X bonds[5] of substituted benzene vapors with the calcium atom, the color of the intial products at 77 K turned green or blue, probably because of the anion radicals of substituted benzenes, depending on the aromatic compounds.

Apparatus. In order to observe directly the anion radicals of substituted benzenes produced by the reactions of the calcium atom with substituted benzene vapors, the apparatus for metal-atom matrix ESR illustrated in Fig. 1 was made. The cryostat assembly attaches directly to the assembly for metal vaporization and is pumped out as part of the complete vacuum system. Metal is vaporized using a filament of tungsten. During the vaporization of the metal, an organic substrate is introduced as vapor through an organic-substrate inlet tube. The co-condensation product of the metal atom and the organic substrate vapor condenses on a stainless-steel drum filled with liquid nitrogen. The co-condensation product of the metal-organic substrate at 77 K is transferred to the ESR tube using a scratching bar.

Miles and his co-workers have recently reported on matrix ESR in a rotating cryostat.[3] The rotating cryostat has been used to deposit the metal atom onto the frozen layer of an organic substrate at 77 K. Our apparatus for the metal atom matrix ESR can similarly and coincidently be used to deposit the co-condensation products formed by the reactions of the metal atom with the organic-substrate vapor.

ESR Studies of Co-Condensation Products of the Calcium Atom and Substituted Benzene Vapors. The co-condensation products of the calcium atom with benzene, alkylbenzenes, and phenyltrimethylsilane respectively were examined by means of ESR. The ESR data of the products of the calcium atom and benzene (No. 1), alkylbenzenes (Nos. 2—5), and phenyltrimethylsilane (No. 6) are summarized in Table 1. Figure 2 shows the ESR spectrum of the product formed by the reaction of the calcium atom with benzene vapor. Although the spectrum is poorly

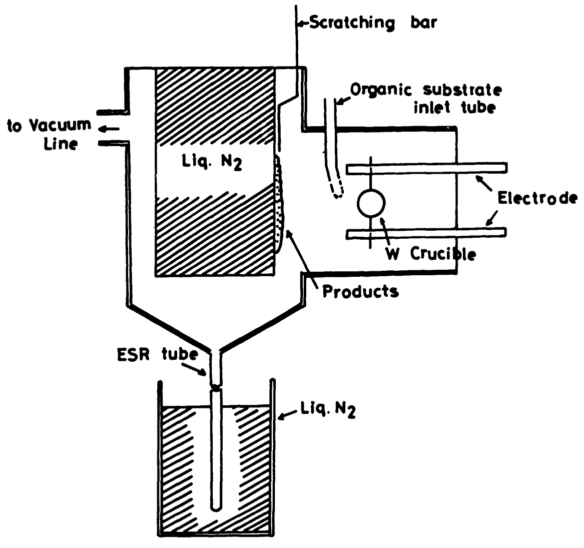


Fig. 1. The apparatus for metal atom matrix ESR.

resolved, it consists of a septet, and the line width is ca. 0.39 mT. The outermost lines of the septet are lost in the noise. The ESR spectrum of the calcium atom-benzene vapor product can safely be assigned to the benzene anion radical by comparison with that of a reference sample.[6,7] The experimental spectrum was reproduced by computer simulation, with the hyperfine splitting constants (hfsc) listed in Table 1. The signal gradually disappeared as the temperature was warmed at 0 °C. Figure 3 shows the ESR spectrum of the product by the reaction of the calcium atom with ethylbenzene vapor. The ESR spectrum is also poorly resolved, and the line width is ca. 0.56 mT. The ESR spectrum of the calcium atom-ethylbenzene vapor product can easily be assigned to the ethylbenzene anion radical by comparison with the ESR data of a reference of sample[6,7] and by computer simulation. The ESR spectra of the products formed by the reactions of the calcium atom with toluene, isopropylbenzene, *t*-butylbenzene, and phenyltrimethylsilane vapors were found to be broad singlets. Such broad singlets may result from the high concentrations of

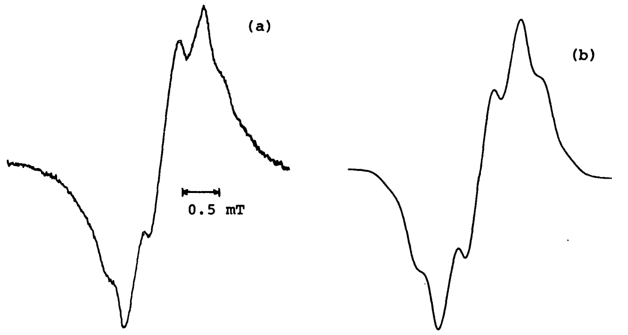


Fig. 2. (a) The observed ESR spectrum of calcium atom-benzene vapor product at −60 °C. (b) Computer simulated spectrum using Lorentzian line shape and a line width of 0.39 mT.

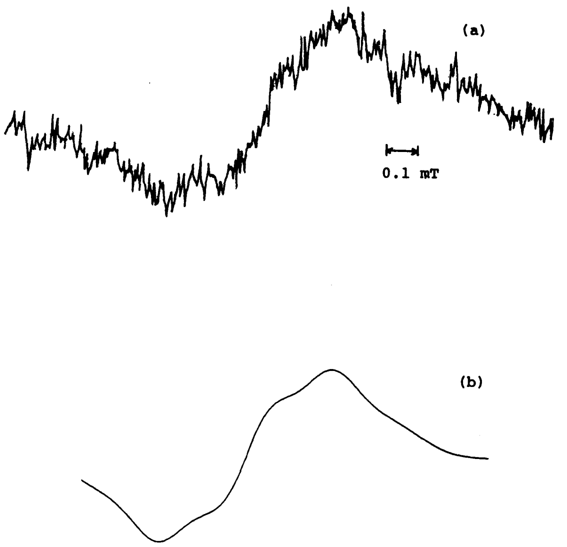
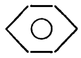
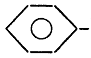
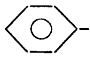
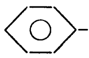
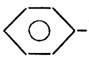
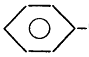


Fig. 3. (a) The observed ESR spectrum of calcium atom-ethylbenzene vapor product at −120 °C. (b) Computer simulated spectrum using Lorentzian line shape and a line width of 0.56 mT.

Table 1. ESR Data for Products of the Calcium Atom with Substituted Benzene Vapors

NO.	Compound	*T*/K	Hfs/mT (ring proton)	*g*[a]	Reference
1		213	0.35 0.404	2.0027 2.0028	This work [6, 7]
2	-Me	153	b) 0.554 (*o*-H), 0.569 (*m*-H) 0.013 (*p*-H)	2.0025 2.0028	This work [6, 7]
3	-Et	153	0.5[c] 0.540 (*o*-H), 0.615 (*m*-H) 0.018 (*p*-H)	2.0031 2.0029	This work [6, 7]
4	-Pr^i	153	b) 0.557 (*o*-H), 0.573 (*m*-H) 0.035 (*p*-H)	2.0030 2.0029	This work [6, 7]
5	-Bu^t	193	b) 0.531 (*o*,*m*-H), 0.172 (*p*-H)	2.0032	This work [6]
6	-SiMe_3	153	b) 0.266 (*o*-H), 0.106 (*m*-H) 0.813 (*p*-H)	2.0034	This work [8]
7	-F	173	b)	2.0035	This work
8	-Cl	173	b)	2.0034	This work

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.

the reaction intermediates or from the matrix conditions. Although no hyperfine structures due to the ring protons were resolved, these signals can safely be assigned to the anion radicals of the corresponding aromatic compounds on the basis of the ESR results for benzene and ethylbenzene vapors-calcium atom described above and on the basis of the reported *g* factors of these anion radicals. As a typical example, Fig. 4 shows the ESR spectrum of the product formed by the reaction of the calcium atom with toluene vapor.

The co-condensation products of the calcium atom with fluorobenzene and chlorobenzene vapors respectively were also examined. The ESR spectra of the products formed by the reactions of the calcium atom with fluorobenzene and chlorobenzene vapors respectively were found to be broader singlets than those of alkylbenzene vapors. The signal for the calcium atom-fluorobenzene vapor product was stable at −60 °C. On the other hand, the signal for the calcium atom-chlorobenzene vapor product was unstable and disappeared even at −60 °C. With bromobenzene, attempts to observe the anion radical failed. Although there have been studies of halogenated aromatic compound anion radicals by means of ESR, there has been no report on *g* factors of fluorobenzene and chlorobenzene anion radicals.[9] No hfs constants of calcium atom-fluorobenzene vapor product or of calcium atom-chlorobenzene vapor product were obtained in this study. Therefore, we could not determine whether the signals obtained by the reactions of the calcium atom with halobenzenes were those of the corresponding anion radicals or not.

These ESR results suggest that the anion radicals of substituted benzenes are produced in the reactions of the calcium atom with substituted benzene vapors.

In this experiment, we made a convenient apparatus for high-boiling metal atom matrix ESR and observed directly by means of ESR anion radicals of substituted benzenes as reaction intermediates in the reactions of the calcium atom with substituted benzene vapors. This apparatus will give further information on reaction intermediates in metal-vapor reactions.

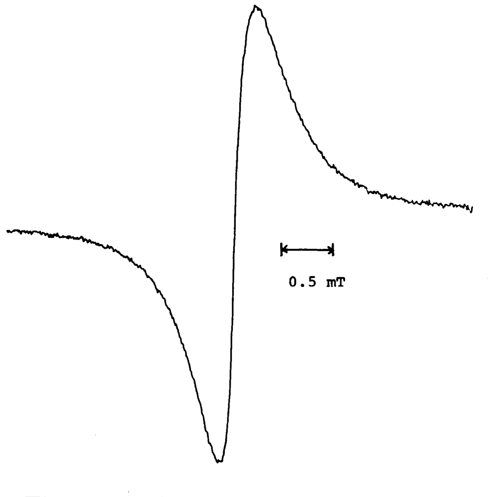


Fig. 4. The observed ESR spectrum of calcium atom-toluene vapor product at −120 °C.

Experimental

ESR Measurements. All the ESR spectra were obtained using a Varian E-9 ESR spectrometer. The field sweep of the spectrometer was calibrated with an aqueous solution of Fremy's salt (a_N=1.307 mT). The *g* factors were determined by reference to that of Fremy's salt (g=2.0055) using a dual cavity.

Materials. Substituted benzenes were dried and distilled prior to use.

Experimental Procedure. As a typical experiment, the reaction of the calcium atom with benzene vapor is described. 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, 1 Torr=133.322 Pa) at a rate of ca. 20 mg min^{-1}. During the vaporization of the calcium metal, benzene (4 cm^3, 45 mmol) was introduced as vapor. The benzene vapor-calcium atom product condensed on a stainless-steel drum filled with liquid nitrogen. The product of calcium atom-benzene vapor at 77 K was transferred to the ESR tube using a scratching bar.

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