ion pairs in a different way. Therefore, one may anticipate that different approaches of measuring solvating power of ethers with respect to alkali ions will in some instances lead to different results.

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Anion Radicals in Liquid Ammonia

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Abstract: Anion radicals have been prepared by alkali metal reduction of various organic substrates in the relatively protic solvent, ammonia. The coupling constants of the anion radicals in ammonia are compared with their values in other solvents. The effects of ion pairing on the esr spectral parameters of the nitrobenzene anion radical **1** are minor.

Liquid ammonia alkali metal (LAAM) solutions have intrigued chemists for many years.[1] The physical properties of LAAM solutions have been studied by many physical methods, including electron spin resonance.[2] More recently, anion radicals have been electrolytically generated and observed by esr in liquid ammonia.[3] We report the formation of anion radicals by reduction of organic substrates with LAAM solutions, followed by their identification with esr. To our knowledge, this report represents the first time that anion radicals have been formed by alkali metal reduction and observed by esr in the relatively protic solvent ammonia.

Experimental Section

Since the esr sample tubes of these ammonia systems are at 11 atm at +30°, it is advised that the necessary safety precautions be considered.

Chemicals were obtained from the following sources: cyclooctatetraene (Chemical Procurement Laboratories), benzophenone (Matheson Coleman and Bell), and nitrobenzene, anthracene, and naphthalene from J. T. Baker. The solids were recrystallized to constant melting point. The liquids were degassed and distilled under high vacuum before use.

The spectra were recorded using the X band of a Varian V-4502-15 esr spectrometer with a 12-in. magnet. Temperature was controlled within ±1° by a Varian V-4557 variable-temperature controller. A copper–constantan thermocouple was used to calibrate the variable-temperature controller.

Coupling constants and line widths were taken directly from the calibrated chart paper.

Ammonia which was dried with potassium metal in bulb a (Figure 1) was distilled into the calibrated bulb b which contained a known amount of alkali metal. An aliquot of the solution in b was then poured into bulb c where it reacted with an equimolar quantity of the organic substrate in liquid ammonia at −78°. The blue color of the LAAM solution was quickly replaced by the color of the anion radical. Several samples having different concentrations of anion radicals were made by taking an aliquot of the anion radical solution into one of the calibrated side arms, d, then distilling liquid ammonia from bulb b into this side arm to the desired concentration and sealing it. Utilizing this procedure, a spectrum of the hydrocarbon anion radical having very narrow lines (40 mG) was obtained.

Results and Discussion

Previous attempts at generating anion radicals in LAAM may not have succeeded due to the fact that the anion radicals became diamagnetic upon addition of excess LAAM and/or some of the anion radicals were unstable at higher temperatures and were reduced by the solvent. Thus, we find that upon addition of more than 1 mol of LAAM/mol of substrate, the spectrum of the anion radical was replaced by the free electron line. Similarly, the napthalene and anthracene anion radicals were not thermally stable above 0°. However, the cyclooctatetraene, benzophenone, and nitrobenzene anion radicals were stable to at least +40°. A reduction of benzene to the anion radical could not be effected, and only the free electron line was observed.

Table I lists the coupling constants of representative anion radicals. The coupling constants of the hydrocarbon anion radicals in liquid ammonia vary no more than 5% from the values recorded in more aprotic solvents such as DME and THF.[4] However, the coupling constants of anion radicals with functional groups are very solvent dependent,[5] particularly if one is comparing data in protic and aprotic solvents. The a_N of the nitrobenzene anion radical **1** has frequently been used to monitor solvent effects.[5] Table II gives the coupling constants of anion radical **1** formed electrolytically or chemically in various solvents. Ion pairing modifies the properties of anion radical **1** in ether solvents,[5d] giving broad, overlapping lines and metal splitting in some instances.[5f] Nitrobenzene reduced by LAAM gives **1**, with a spectrum (Figure 2) similar

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[1] (a) W. L. Jolly and C. J. Hallada, "Non-aqueous Solvent Systems," T. C. Waddington, Ed., Academic Press Inc., New York, N. Y., 1965, p 1; (b) G. Lepoutre and M. J. Sienko, "Metal-Ammonia Solutions," W. A. Benjamin, Inc., New York, N. Y., 1964.

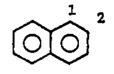
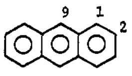
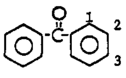
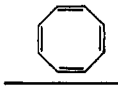
[2] P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier Publishing Co., New York, N. Y., 1967, p 43.

[3] (a) D. H. Levy and R. J. Myers, *J. Chem. Phys.*, **41**, 1062 (1964); **43**, 3063 (1965); **44**, 4177 (1966); (b) D. H. Levy, Ph.D. Thesis, University of California, 1965; (c) T. J. Katz and C. Talcott, *J. Amer. Chem. Soc.*, **88**, 4732 (1966); (d) D. H. Levy and R. J. Myers, *J. Chem. Phys.*, **42**, 3731 (1965).

[4] K. W. Bowers, *Advan. Mag. Resonance*, **1**, 317 (1965).

[5] (a) L. H. Piette, P. Ludwig, and R. N. Adams, *J. Amer. Chem. Soc.*, **83**, 3909 (1961); (b) P. Ludwig, T. Layloff, and R. N. Adams, *ibid.*, **86**, 4568 (1964); (c) J. Gendell, J. H. Freed, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2832 (1962); (d) R. L. Ward, *ibid.*, **30**, 852 (1959); (e) J. E. Harriman and A. H. Maki, *ibid.*, **39**, 778 (1963); (f) R. L. Ward, *J. Amer. Chem. Soc.*, **83**, 1296 (1961).

Table I. Coupling Constants of Hydrocarbon Anion Radicals

Compound	Metal	Solvent	Temp, °C	a_1	a_2	a_{other}	Ref
	K	NH_3	−50	5.02	1.88		This work
	K	THF	Room temp	4.95	1.87		*a*
	Na	THF	+22.5	4.90	1.83	1.05 (Na)	*b*
	K	NH_3	−50	2.78	1.51	5.56	This work
	K	DME	...	2.726	1.513	5.346	*c*
	K	THF	Room temp	2.74	1.51	5.56	*a*
	K	NH_3	−50	2.63	0.84	3.48	This work
	K	DME	+20	2.53	0.84	3.45, 0.39 (K)	*d*
	Na	DME	+20	2.58	0.86	3.44, 1.125 (Na)	*d*
	K	NH_3	+22	3.28			This work
	Li	THF	+22	3.209			*e*

[a] A. Carrington, F. Dravnieks, and M. C. R. Symons, *J. Chem. Soc.*, 947 (1959). [b] N. M. Atherton and S. I. Weissman, *J. Amer. Chem. Soc.*, **83**, 1330 (1961). [c] J. R. Bolton and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 3307 (1964). [d] P. B. Ayscough and R. Wilson, *J. Chem. Soc.*, 5412 (1963). [e] H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *J. Amer. Chem. Soc.*, **85**, 2360 (1963).

Table II. Coupling Constants of Nitrobenzene Anion Radicals

Metal	Solvent	Temp, °C	a_N	a_o	a_m	a_p	Ref
Li	NH_3	−50	10.40	3.25	1.03	3.83	This work
Na	NH_3	−50	10.63	3.24	1.03	3.82	This work
K	NH_3	−50	10.62	3.23	1.03	3.84	This work
Alkaline dithionite	H_2O	Room temp	13.30	3.40	0.90	3.40	7b
Electrolytic	CH_3CN	...	10.32	3.39	1.09	3.97	6
Electrolytic	DMF	...	10.33	3.46	1.13	3.86	7a
Electrolytic	DMSO		9.87	3.37	1.07	4.02	5e

to that from the electrolytic reduction.[6] The effects of ion pairing on the esr spectral parameters of **1** appear to be minor. Very small changes are observed in the hfs line widths and the coupling constants of **1** as its concentration is varied from 10^{-4} to 10^{-2} *M*, or if the ammonia solution is made 0.4 *M* in KI. We also find the coupling constants of **1** are independent of temperature from −78 to −30°, and independent of counterion for $M^+ = Li^+, Na^+, K^+$. The electrolytic reduction in liquid ammonia[3d] with sodium iodide as carrier electrolyte leads to coupling constants slightly different from ours. The coupling constants of **1** formed by LAAM are very similar to those for **1** generated electrolytically in DMF[7a] and acetonitrile[6] and are not too different for **1** generated electrolytically in the solvents water[7b] and DMSO.[5e] Ion pairing dramatically influences the physical properties of the cyclooctatetraene anion radical in liquid ammonia.[8] The effects of ion pairing on the coupling constants of **1** in liquid ammonia appear to be very minor.

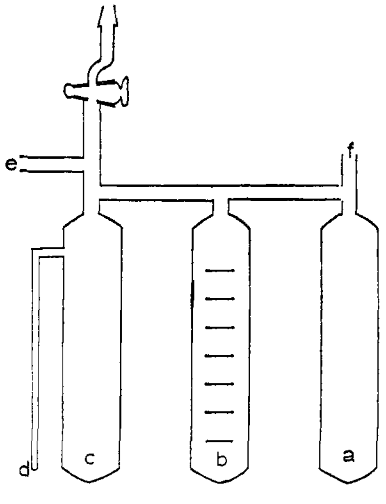


Figure 1. High-vacuum apparatus for generating anion radicals in liquid amonia. e and f allow addition of metal and substrate. They are subsequently sealed.

Figure 2. First-derivative esr spectrum of the anion radical of nitrobenzene reduced by K in liquid ammonia at −50°. (Arrow indicates a 10-G separation.)

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(6) A. H. Maki and D. H. Geske, *J. Amer. Chem. Soc.*, **83**, 1852 (1961).

(7) (a) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960); (b) P. L. Kolker and W. A. Waters, *J. Chem. Soc.*, 1136 (1964).

(8) (a) F. J. Smentowski and G. R. Stevenson, submitted for publication; (b) *J. Phys. Chem.*, in press.