

Hall Effect in Concentrated Metal-Ammonia Solutions¹

Sir:

We have measured the Hall coefficient in solutions of Li and Na in liquid NH₃. The concentration range covered was from 1.0 mole % (0.5 M) to saturation; the temperature range was from -80 to -40°. The Hall coefficient, R_H , provides a direct measure of the concentration of unbound (free) electrons. If the free electrons are treated as an electron gas then one finds

$$R_H = (ne)^{-1}$$

where e is the electron charge and n is the concentration of electrons in cm.⁻³. One may also write $R_H = 10^3 \cdot (M_e F)^{-1}$ where M_e is the electron molarity and F is the faraday.

We find that the carrier of electricity in the solution is negatively charged and may safely be presumed to be the electron. At concentrations above 5 mole % (1.8 M), we find almost one free electron per metal atom. In this range, then, the material is metallic in character. As the concentration is decreased below 5 mole %, the free electron concentration drops very rapidly, so that one finds only one free electron per 1000 metal atoms when the concentration of metal atoms is near 2 mole %. Representative data are displayed in Table I.

TABLE I
HALL COEFFICIENTS

Metal	Concn., mole %	Temp., °C.	Measured R_H , m ² /coulomb	Density, ^a g./ml.	Calculated R_H , m ² /coulomb	
Li	Saturated	-65	1.70×10^{-9}	0.492	1.50×10^{-9}	
	17.4	-65	1.87×10^{-9}	0.520	1.75×10^{-9}	
	15.5	-65	2.16×10^{-9}	0.536	1.93×10^{-9}	
	12.5	-65	2.74×10^{-9}	0.558	2.35×10^{-9}	
	6.9	-62	4.28×10^{-9}	0.622	3.96×10^{-9}	
	4.85	-61	6.83×10^{-9}	0.649	5.45×10^{-9}	
	3.22	-61	93.4×10^{-9}	0.669	8.04×10^{-9}	
	2.30	-61	7.17×10^{-6}	0.682	11.1×10^{-9}	
	1.52	-61	41.9×10^{-6}	0.692	16.7×10^{-9}	
	1.33	-65	$444. \times 10^{-6}$	0.695	19.0×10^{-9}	
	Na	8.83	-63	2.53×10^{-9}	0.630	3.22×10^{-9}
		6.25	-44	6.36×10^{-9}	0.641	4.45×10^{-9}
		4.38	-40	10.3×10^{-9}	0.654	6.24×10^{-9}
1.65		-55	860×10^{-9}	0.693	15.5×10^{-9}	
1.00		-50	73.7×10^{-6}	0.693	25.8×10^{-9}	
0.51		-44	1.8×10^{-3}	0.690	50.2×10^{-9}	
0.51		-63	1.5×10^{-3}	0.712	49.8×10^{-9}	
0.34		-65	1.3×10^{-3}	0.717	73.7×10^{-9}	

^a Densities were obtained by interpolation and extrapolation from the data of W. C. Johnson, A. W. Meyer, and R. D. Martens, *J. Am. Chem. Soc.*, **72**, 1842 (1950), and S. Kikuchi, *J. Soc. Chem. Ind. Japan*, **47**, 488 (1944).

The observation of one free electron per metal atom at saturation is consistent with the reflectivity found by Beckman and Pitzer² and is also consistent with the crude Hall measurements of Jaffé.³ The rapid rise of electron concentration in the 1-5 mole % range has not been heretofore observed. The fact that the free electron concentration changes by 10³ while the metal concentration changes by only 2 is difficult to explain. A rapid onset of a metallic state must be taking place. In the absence of spectral data, one cannot assign the identity of the electron traps at the low concentrations.

(1) Assisted by the Office of Naval Research and the Robert A. Welch Foundation.

(2) T. A. Beckman and K. S. Pitzer, *J. Phys. Chem.*, **65**, 1527 (1961).

(3) H. Jaffé, *Z. Physik*, **93**, 741 (1935).

The bound (nonfree) electrons might exist either as solvated electrons or with metal atoms as "monomers."

The measurements were made using an alternating magnetic field and an alternating current. The samples were prepared in glass cells with tungsten electrodes. Dry NH₃ was distilled onto preweighed metal. The Na had been distilled; the Li was simply cut under oil, washed with petroleum ether, and dried in a helium stream. The solutions were mixed by bubbling helium gas through them. Decomposition was slight in the Li solutions over periods of several days. The Na solutions were somewhat less stable but still were stable enough to be diluted several times. Calculated concentrations were in agreement with measured conductivities and with the various phase boundaries encountered.

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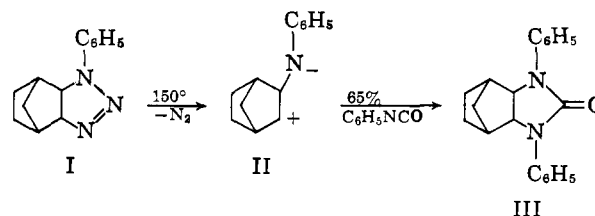
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Cycloadditions. The Reactions of Δ^2 -1,2,3-Triazolines with Phenyl Isocyanate and Phenyl Isothiocyanate¹

Sir:

While great heuristic success has been achieved through the development of a unified theory for "1,3-dipolar cycloadditions,"² certain mechanistic aspects of these reactions still seemed inadequately defined and demanding of careful examination. While seeking examples of "1,3-dipolar cycloadditions" amenable to close mechanistic scrutiny, we investigated the decomposition of the norbornene-phenyl azide adduct, *exo*-3-phenyl-3,4,5-triazatricyclo[5.2.1.0^{2,6}]dec-4-ene (I), in the presence of phenyl isocyanate. This reaction has been described^{2,3} as proceeding by unimolecular thermal elimination of nitrogen to give a 1,3-dipolar species (II) which adds to phenyl isocyanate to give the diphenylurea III.



In the present study, the triazoline I and an excess of phenyl isocyanate in *o*-dichlorobenzene at 160° gave colorless C₂₀H₂₀N₂O (*Anal.* Found: C, 78.69; H, 6.62; N, 9.19) of m.p. 162° (60% after two recrystallizations from cyclohexane); ν_{\max}^{KBr} 1700 cm.⁻¹; $\lambda_{\max}^{\text{EtOH}}$ 245 m μ (log ϵ 4.4). The n.m.r. spectrum of the adduct shows aromatic protons at τ 2.4-3.4 (10 H), a quartet at 4.7 (1 H), a quartet at 6.0 (1 H), a multiplet at 7.2-7.6 (2 H), and complex absorption at 8.0-

(1) Supported in part by the Petroleum Research Fund, administered by the American Chemical Society.

(2) R. Huisgen, *Angew. Chem., Intern. Ed. Engl.*, **2**, 565 (1963); *ibid.*, **2**, 633 (1963), and references cited therein.

(3) R. Huisgen, "Theoretische Chemie und Organische Synthesen. Festschrift der Zehnjahresfeier des Fonds der Chemischen Industrie. Düsseldorf, 1960.