Hall Effect in Concentrated Metal–Ammonia Solutions[1]

Sir:

We have measured the Hall coefficient in solutions of Li and Na in liquid NH_3. 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 $R_H = 10^3 \cdot (M_eF)^{-1}$ 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, m³/coulomb	Density,[a] g./ml.	Calculated R_H, m.³/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 Pitzer[2] 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 10^3 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. 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 NH_3 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.

Acknowledgment.—The authors are deeply indebted to the technical skill of C. Yates for the success of the experiment.

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RECEIVED AUGUST 19, 1964

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[1] Assisted by the Office of Naval Research and the Robert A. Welch Foundation.

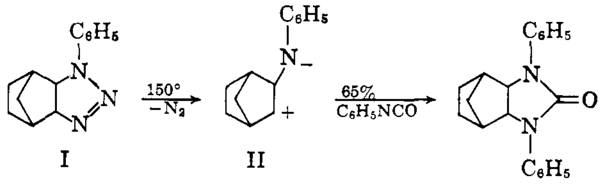
[2] T. A. Beckman and K. S. Pitzer, *J. Phys. Chem.*, **65**, 1527 (1961).

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

Cycloadditions. The Reactions of Δ²-1,2,3-Triazolines with Phenyl Isocyanate and Phenyl Isothiocyanate[1]

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.



I II III

In the present study, the triazoline I and an excess of phenyl isocyanate in *o*-dichlorobenzene at 160° gave colorless $C_{20}H_{20}N_2O$ (*Anal.* Found: C, 78.69; H, 6.62; N, 9.19) of m.p. 162° (60%, after two recrystallizations from cyclohexane); $\nu_{\max}^{\text{KBr}}$ 1700 cm.$^{-1}$; $\lambda_{\max}^{\text{EtOH}}$ 245 mμ (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–

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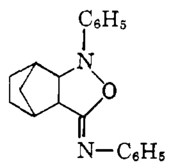
[1] Supported in part by the Petroleum Research Fund, administered by the American Chemical Society.

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

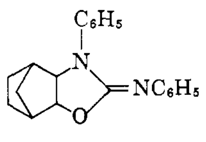
[3] R. Huisgen, "Theoretische Chemie und Organische Synthesen, Festschrift der Zehnjahresfeier des Fonds der Chemischen Industrie, Düsseldorf, 1960.

8.8 (6 H). These n.m.r. data rigorously exclude III from further consideration as a structure for the major isolable product.

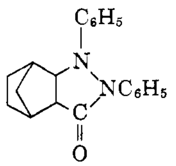
Reduction of the product $C_{20}H_{20}N_2O$ with lithium aluminium hydride[4] gave a colorless oil, $C_{20}H_{22}N_2$, which was purified by v.p.c. (*Anal.* Found: C, 82.10; H 7.71) and had no carbonyl band in the infrared. Thus cycloadducts such as IV and V are also eliminated as structures for the product.



IV



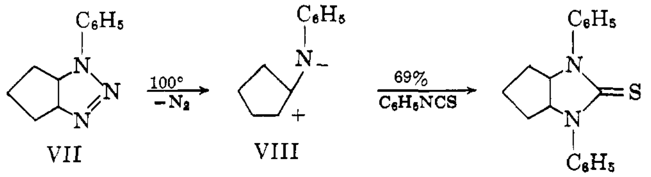
V



VI

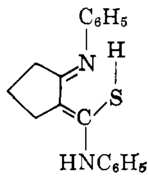
While the 3-pyrazolidone VI is the structure most consistent with the spectral[5] and chemical evidence that can be formally derived from II and phenyl isocyanate by a cycloaddition, it may not be assigned to the product at present.

The reaction of the cyclopentene–phenyl azide adduct, 2-phenyl-2,3,4-triazabicyclo[3.3.0]oct-3-ene (VII), with phenyl isothiocyanate has also been represented as a "1,3-dipolar cycloaddition."[3]

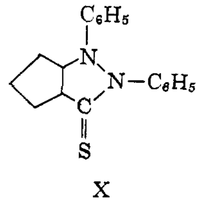


IX

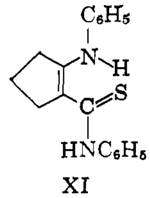
When it became clear that the reaction of the norbornene–phenyl azide adduct with phenyl isocyanate does not follow an analogous pathway, the thermal decomposition of VII in the presence of phenyl isothiocyanate was reinvestigated. The major product from the reaction is neither the thiourea IX nor the 3-thiopyrazolidone X, but rather the thioanilide XI.[6]



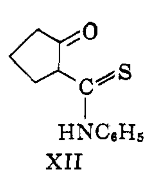
XI′



X



XI



XII

The triazoline VII with an excess of phenyl isothiocyanate in chlorobenzene at 110° gave the product $C_{18}H_{18}N_2S$ [*Anal.* Found: C, 73.36; H, 6.12; N, 9.39; mol. wt., 296 (osmometric in benzene)] as bright yellow needles, m.p. 128.5–130.5° (78% yield, from cyclohexane); $\nu_{\max}^{\mathrm{CHCl_3}}$ 3390, 1612, 1595, 1580, 1500, 1390, and 1250 cm.$^{-1}$ strong; $\lambda_{\max}^{\mathrm{CHCl_3}}$ 386 (ϵ 24,000) and 314 mμ (ϵ 9000). The n.m.r. spectrum of a solution of the product in deuteriochloroform had absorption at τ −3.0 (1 H), 2.0–3.4 (11 H), a multiplet centered at 7.25 (4 H), and a multiplet centered at 8.15 (2 H).

The infrared, ultraviolet, and n.m.r. spectral data are all incompatible with structure IX.[7] The spectral data may, however, be rationally correlated with an alternate structural proposal, the thioanilide XI. In particular, the 3390 cm.$^{-1}$ band in the infrared and the τ −3.0 proton in the n.m.r. spectra may be assigned to the NH proton of XI, hydrogen bonded to sulfur.[6]

Conclusive evidence in favor of structure XI was obtained by hydrolysis of the product $C_{18}H_{18}N_2S$ with 70% sulfuric acid to aniline and β-ketothioanilide XII. The hydrolysis product proved identical with an independently synthesized[8] authentic sample of XII as judged by melting point, mixture melting point, and infrared and n.m.r. spectral criteria.

This reaction of triazoline VII may involve 1-anilinocyclopentene as an intermediate,[8,9] or some more complex mechanism may obtain. It is clear that, at least in our hands, the reaction is no cycloaddition, and that seemingly modest variations in structure, as between the cyclopentene- and norbornene–phenyl azide adducts and between phenyl isothiocyanate and phenyl isocyanate, can divert one high-yield process to alternative modes of behavior. That the reaction of I with phenyl isocyanate involves the dipole II as an intermediate appears extremely doubtful. Preliminary work indicates that the rate of nitrogen evolution from I depends on the phenyl isocyanate concentration.

Whether or not our products VI, m.p. 162°, and XI, m.p. 128.5–130.5°, and those isolated by earlier workers[2,3] and assigned structures III and IX are identical remains to be seen.[10] Kinetic studies of these and similar reactions are in progress.

The present results strongly suggest that "1,3-dipolar cycloadditions" may be less mechanistically homogeneous than has been previously supposed.

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[4] Compare R. L. Hinman, *J. Am. Chem. Soc.*, **78**, 1645 (1956).

[5] B. J. R. Nicolaus, *et al.*, *Helv. Chim. Acta*, **44**, 2055 (1961).

[6] Possible tautomerization between XI and XI′ is here neglected.

[7] For N,N′-diphenylthiourea, $\lambda_{\max}^{\mathrm{EtOH}}$ 272 mμ (log ϵ 4.32); M. G. Ettlinger and J. E. Hodgkins, *J. Am. Chem. Soc.*, **77**, 1831 (1955).

[8] W. Reid and W. Käppeler, *Ann.*, **673**, 132 (1964).

[9] G. A. Berchtold, *J. Org. Chem.*, **26**, 3034 (1961); S. Hünig, K. Hübner, and E. Benzing, *Chem. Ber.*, **95**, 926 (1962); R. Fusco, G. Bianchetti, and S. Rossi, *Gazz. chim. ital.*, **91**, 825 (1961).

[10] In ref. 2 and 3, credit for these cycloaddition products is given to unpublished research of R. Huisgen and R. Grashey, Munich, 1959–1960; unfortunately, no melting points or spectral data for the adducts "III" and "IX" are given.

[11] National Science Foundation Undergraduate Research Participant.

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RECEIVED AUGUST 24, 1964

The Influence of Unsaturation and of Fluorine Substitution on Ketone–Alcohol Equilibrium Constants. A Measure of α,β-Unsaturated Ketone Resonance Energy and of Halogen Destabilization[1]

Sir:

The destabilization of a carbonyl group by a halogen atom located α to a saturated ketone or α, β, or γ to

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[1] Supported in part by Grant F-185, American Cancer Society, and A-4044, National Institutes of Health.