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## Reduction of Benzene by Europium and Ytterbium

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Alkali and alkaline earth metals dissolve in liquid ammonia forming blue solutions of solvated electrons and metal cations.[1] It is interesting that the physical and inorganic chemical properties of europium and ytterbium resemble those of the alkaline earth metals.[2,3] These unique rare earth elements also dissolve in ammonia.[2] Optical and electron spin resonance spectroscopy studies indicate that blue ammonia solutions of europium contain solvated electrons and europium(II) cations.[4] The objective of the present investigation has been to determine whether ammonia solutions of europium or ytterbium are comparable to those of alkali or alkaline earth metals for a typical reduction reaction.

With protonic materials (water, alcohols, etc.) added, alkali and alkaline earth metals in refluxing ammonia ($\sim -33°$) are excellent reagents for the reduction of benzene (Birch reaction).[5] Under these "Birch conditions,"[5] ytterbium reduced benzene mainly to 1,4-cyclohexadiene (expt 5, Table I). No observable reaction occurred in refluxing, neat ammonia until ethanol was added. These results are completely analogous to those obtained with the alkali metals.[5]

Benzene can be reduced by alkali and alkaline earth metals in neat, liquid ammonia without the added acids, provided elevated temperatures (60–130°) are employed.[6] The ammonia serves as the required acid and, consequently, metal amides are the inorganic products. The organic products obtained depend somewhat upon the metal employed. Therefore, it seemed of interest to reduce benzene with europium and ytterbium in neat ammonia to see if their reducing properties resemble those of certain group I or II metals more than those of others. Both europium (expt 1) and ytterbium (expt 2–4) in neat ammonia at 40–100° reduced benzene to a mixture of cyclohexadienes and cyclohexene. Under similar conditions, sodium and potassium produced exclusively cyclohexene whereas calcium and lithium yielded a mixture of cyclohexene and cyclohexadienes.[6] It appears that the two rare earth metals behave like calcium or lithium rather than sodium or potassium for this reduction. Europium amide and ytterbium amide were isolated in expt 1 and 2, respectively, after the excess ammonia and hydrocarbons had been removed by distillation. These high-melting solids, which were not purified further, analyzed more nearly for $Eu(NH_2)_2$ and $Yb(NH_2)_2$ than for $Eu(NH_2)_3$ and $Yb(NH_2)_3$.

The two metals, samarium and gadolinium, adjacent to europium in the periodic series were tested and found to be totally ineffectual for the reduction of benzene in neat ammonia at elevated temperatures (expt 6 and 7). The metals were recovered unchanged.

TABLE I

REDUCTION OF BENZENE IN LIQUID AMMONIA[a]

| Expt no. | $C_6H_6$, moles | Metal,[b] g-atoms | $NH_3$ or $C_2H_5OH$, moles | Temp, °C | Time, hr | Product composition, %[c] | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | |  |  |  |  |
| 1 | 0.05 | Eu<br>0.037 | $NH_3$<br>1.5 | 60 | 8 | 45.4 | 10.5 | 14.6 | 29.5 |
| 2 | 0.1 | Yb<br>0.13 | $NH_3$<br>2.6 | 40 | 3.8 | 2.3 | 14.5 | 38.2 | 45.1 |
| 3 | 0.1 | Yb<br>0.13 | $NH_3$<br>2.7 | 80 | 2.5 | 15.6 | 39.4 | 28.9 | 16.1 |
| 4 | 0.1 | Yb<br>0.13 | $NH_3$<br>2.7 | 100 | 1.3 | 0.6 | 55.9 | 26.7 | 16.8 |
| 5 | 0.12 | Yb<br>0.13 | $NH_3$<br>10.0<br>$C_2H_5OH$<br>0.86 | −33 | 3.5 | 0 | 1.4 | 0 | 98.6 |
| 6 | 0.06 | Sm<br>0.08 | $NH_3$<br>1.2 | 115 | 2.8 | 100 | 0 | 0 | 0 |
| 7 | 0.08 | Gd<br>0.11 | $NH_3$<br>2.0 | 70 | 2 | 100 | 0 | 0 | 0 |

[a] An autoclave was employed for all experiments except 5. A glass flask was used for the latter. [b] All of the metal reacted in expt 1–5. None of the samarium and gadolinium reacted in expt 6 and 7. [c] Normalized values. The product material balances were 97–99.5% except that for expt 5 which was 76.3%.

### Experimental Section

High-purity (>99%) samarium, europium, gadolinium, and ytterbium metals were purchased from American Potash Co. The high-purity benzene was distilled from lithium aluminum hydride.

For the elevated temperature experiments with neat liquid ammonia, a 300-ml, stainless steel Magnadrive autoclave was employed. It was loaded inside a nitrogen-flushed drybox with benzene and the metal. Outside of the drybox, ammonia was

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[1] M. C. R. Symons, *Quart. Rev.* (London), **13**, 99 (1956).

[2] J. C. Warf and W. L. Korst, *J. Phys. Chem.*, **60**, 1590 (1956), and references cited therein.

[3] W. Klemm, H. Kock, and W. Mühlpfordt, *Angew. Chem. Intern. Ed. Engl.*, **3**, 704 (1964), and references cited therein.

[4] R. Catterall and M. C. R. Symons, *J. Chem. Soc.*, 3763 (1965).

[5] A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950); **12**, 17 (1958).

[6] L. H. Slaugh and J. H. Raley, *J. Org. Chem.*, **32**, 369 (1967).

distilled before being introduced into the autoclave from a weighed stainless steel vessel of ~250-ml capacity. The autoclave was then heated and the contents were stirred with a paddle speed of ~1000 rpm (see Table I for conditions and reaction times). After reaction was complete, the system was cooled to room temperature and the excess ammonia was allowed to evaporate through a toluene scrubber. A vacuum was applied through the scrubber to the autoclave and the organic product was distilled into the cooled solvent. The organic products were determined quantitatively by glpc (see Table I) and identified by infrared and mass spectrometric analyses. Hydrocarbon material balances were 97–99.5%.

Crude ytterbium amide remaining after distillation of ammonia and the organic products in expt 2 was a lavender-brown solid which when heated in a closed capillary tube became yellow at 400° and orange at 425° without melting. The ytterbium content of the amide was determined by neutral activation analysis.

*Anal.* Calcd for $Yb(NH_2)_2$: Yb, 84.4; N, 13.6; H, 2.0. Calcd for $Yb(NH_2)_3$: Yb, 78.3; N, 19.0; H, 2.7. Found: Yb, 82.8; N, 13.6; H, 2.3; C, 0.6.

Europium amide collected similarly from expt 1 was a gold-colored solid with mp >425°. The europium content of the amide was determined by neutron activation analysis.

*Anal.* Calcd for $Eu(NH_2)_2$: Eu, 82.6; N, 15.2; H, 2.2. Calcd for $Eu(NH_2)_3$: Eu, 76.0; N, 21.0; H, 3.0. Found: Eu, 82.6; N, 12.6; H, 2.3; C, 1.8.

The reduction of benzene under "Birch conditions" (expt 5) was performed at atmospheric pressure in a round-bottom flask equipped with a stirrer, gas-inlet tube, and Dry Ice condenser. The flask containing 0.13 g-atom of ytterbium turnings was cooled in a Dry Ice–acetone bath and ~250 ml of liquid ammonia was introduced by distillation. The dark solution was allowed to warm to the reflux temperature of ammonia (~−33°) and then 0.12 mole of benzene was injected. After 3.5 hr of stirring, the solution still remained dark indicating that little reaction had occurred. Ethanol (0.86 mole) was added and the mixture turned reddish brown. *n*-Pentane was added and the flask was allowed to warm to evaporate the ammonia. Water and then 10% hydrochloric acid were added to dissolve the solid. The hydrocarbon layer was separated, washed with water, dried over calcium chloride, and analyzed by glpc. The normalized product composition is listed in Table I. The material balance for the organic products was only 76.3%. This indicates that some material was lost during the evaporation of the ammonia and the extraction process.

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# Correspondence

## Intramolecular Isomerization of Octahedral Complexes by Mechanisms Not Involving Bond Rupture

*Sir:*

Two intramolecular isomerization mechanisms for octahedral complexes that do not involve bond rupture have been suggested.[1,2] These were originally proposed for chelate compounds and will be referred to hereafter as the Rây and Dutt and the Bailar twists, respectively.

The Rây and Dutt twist for a simple tris chelate complex is shown in Figure 1. If one of the rings is imagined to remain fixed in space, the motion can be described as the rotations of the remaining two rings 90° in opposite directions about axes perpendicular to their respective planes and passing through the metal ion. The rings remain rigid throughout the twisting process with the ring donor–metal–donor (D–M–D) bond angles remaining constant at approximately 90°. This motion is seen to result in optical inversion. The designations of absolute configuration used in this discussion are those of Piper[3] and Legg and Douglas.[4]

The Bailar twist for the same molecule as viewed along the $C_3$ axis is pictured in Figure 2. The motion of this mechanism may be described as the rotation of the three metal–donor bonds extending down from the plane of the paper (dotted lines) 120° about the $C_3$ axis in a counterclockwise direction. There results a contraction of the ring D–M–D bond angles ($\alpha$) and consequent distortion of the chelate rings in the transition state. If this contraction is too great, the angle can expand back to a more favorable value only at the expense of the adjacent D–M–D angles ($\beta$) between donors in different rings. For the situation in which all D–M–D bond angles are equal in the trigonal prismatic transition state (*i.e.*, $\alpha = \beta$), values of 81° 48′ are required.[5] This motion also results in optical inversion.

An important difference, then, is seen to exist between the Rây and Dutt and the Bailar twists as originally proposed. In the former, the chelate ring internal angles do not change throughout the transformation, but do in the latter. In addition, in Bailar's mechanism, all of the nonring D–M–D bond angles ($\beta$) change, while in the Rây and Dutt motion those angles ($\omega$) between bonds in the rotating rings change but other nonring angles remain fixed. In the mechanism pictured in Figure 1, the dihedral angle between the planes of the rotating rings always remains 90°, but the nonring angles ($\omega$) between donor–metal bonds in these rings decrease in the transition state.[6]

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[1] P. Rây and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943).

[2] J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958). This mechanism was also proposed independently by W. G. Gehman (Ph.D. Thesis, Pennsylvania State University, State College, Pa., 1954), and L. Seiden (Ph.D. Thesis, Northwestern University, Evanston, Ill., 1957).

[3] T. S. Piper, *J. Am. Chem. Soc.*, **83**, 3908 (1961).

[4] J. I. Legg and B. E. Douglas, *ibid.*, **88**, 2697 (1966).

[5] It is interesting to note that the first three-dimensional X-ray data (R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **5**, 411 (1966)) on a trigonal prismatic compound, $Re(S_2C_2(C_6H_5)_2)_3$, reveal chelate ring angles (*i.e.*, $\alpha$) of 81.9, 81.5, and 80.9°, in remarkably close agreement with the value calculated by Bailar[2] for the trigonal prismatic transition state having equal D–M–D bond angles. The value originally given was 81° 10′; more refined calculations yield the value 81° 48′.