

The C-S distance of 1.70 Å. is close to the mean of the values 1.62–1.75 Å. found in the rhenium complex.⁴ We consider the geometry of the dithioglyoxal ligands in MoS₆C₆H₆ as the ultimate result of the accumulation of negative charge in the ligands. In agreement with general ideas of the bonding in complexes of this type outlined previously,³ it must be pointed out that in C_{3h} as well as D_{3h} symmetry several of the σ- and π-bonding interactions fall into the same irreducible representations. The complexes are, therefore, three-dimensionally delocalized. Owing to the presence of low-lying π molecular orbitals in the isolated dithioglyoxal ligands, the highest occupied MO's in the complex, which belong to the symmetry E', are localized both on the metal and the ligands but have predominantly ligand character. The occupation of this orbital will thus cause the ligands to resemble more closely dithiolato dianions; consequently, the C=S bond lengths are found similar to those in thiophene (observed¹⁰ 1.71g Å.), while the C-C bond distances appear to be equal to conventional double bonds. The significant ligand character of the highest-occupied E'-type MO may, in addition, force the sulfur atoms into a state between sp² and sp³ hybridization, which could receive additional stabilization through intermolecular packing effects. In the infrared spectrum (in KBr), C=C and C=S stretching vibrations are observed at 1401 and 1121 cm.⁻¹ and 857 cm.⁻¹, indicating a significant perturbation of these bonds; the C-H stretch appears in the expected olefinic region (3033 cm.⁻¹, in KBr). With this new interpretation of the bonding in these complexes it becomes also possible to assign a formal oxidation number to the central metal atoms. In the case of group VI transition metal complexes, the E'-type MO is fully occupied, leading to the oxidation number of +4. In view of the covalent nature of bonding in these compounds, this number has of course only formal significance. Full details of this theoretical evaluation will be presented in an extensive publication.

(10) B. Bak, D. Christensen, J. Rastrup-Andersen, and E. Tannenbaum, *J. Chem. Phys.*, **25**, 892 (1956).

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Kinetics of the Lithium-Ammonia-Ethanol Reduction of Benzene. A Fourth-Order Reaction¹

Sir:

Reduction of benzene to 1,4-dihydrobenzene by alkali metal and alcohol in ammonia solution was first reported by Wooster in 1939.² Hypotheses for the mechanism of this reaction and analogous reductions of numerous other aromatic substrates have commonly involved either (A) stepwise addition of two electrons to the substrate, forming in turn a radical anion and a

(1) Paper V in the series Reactions of Metal-Ammonia Solutions. For paper IV see *J. Am. Chem. Soc.*, **85**, 3530 (1963).

(2) C. B. Wooster, U. S. Patent 2,182,242 (1939); *Chem. Abstr.*, **34**, 1993 (1940). Cf. also C. B. Wooster and K. L. Godfrey, *J. Am. Chem. Soc.*, **59**, 596 (1937).

dianion, which picks up two protons, or (B) protonation of the intermediate radical anion to yield a radical which picks up the second electron and proton.³ These hypotheses have been based almost exclusively on product analysis, *i.e.*, rationalizations of specific products from reduction of various substrates. This type of analysis gives little insight into the many possible details of A or B, or even into a choice between them. Kinetic analysis, which should give much better insight, has been little used, presumably because of general experimental difficulties with metal-ammonia solutions and because of complications arising from an omnipresent reaction of the alkali metals which competes with substrate reduction. This competing reaction is hydrogen evolution. Previous papers in this series on metal-ammonia solutions reported successful kinetic analyses of the hydrogen evolution reaction, from both alcohol⁴ and ammonia itself,¹ and we now wish to report the kinetic analysis of reduction of benzene by lithium and ethanol (eq. 1).



Our results are quite different from those of the one previous kinetic analysis of this important reaction; in 1959 Krapcho and Bothner-By reported that the rate law for (1) is third order over-all, first order in each of the three reactants.⁵ Our rate data on reduction 1 were gathered using the same basic experimental techniques as Krapcho and Bothner-By,⁶ but our data plotted according to the linear form of their third-order rate law give smooth curves. At first it was thought this difficulty could be attributed simply to the competing hydrogen evolution,⁹ which they ignored. By use of lithium (rather than the more reactive sodium and potassium) and carefully purified ammonia,⁶ competition due to hydrogen evolution from the solvent can be ignored, but reaction of lithium and ethanol (2) can



still be competitive.¹⁰ However, two far more funda-

(3) Cf. (a) A. J. Birch, *Quart. Rev. (London)*, **4**, 69 (1950); **12**, 17 (1958); (b) H. Smith, "Organic Reactions in Liquid Ammonia," Interscience Publishers, Inc., New York, N. Y., 1963, pp. 237-279; (c) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, pp. 61-71; (d) A. Streitwieser, "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 425 ff.

(4) E. J. Kelly, H. V. Secor, C. W. Keenan, and J. F. Eastham, *J. Am. Chem. Soc.*, **84**, 3611 (1962).

(5) A. P. Krapcho and A. A. Bothner-By, *ibid.*, **81**, 3658 (1959).

(6) The only distinction of our techniques would appear to be in refinement. Immediately prior to use, anhydrous ammonia was distilled through BaO into our equipment, which could be used in such a manner as to prevent introduction of unwanted metallic⁷ and gaseous⁸ catalysts. This equipment allowed rapid mixing of homogeneous ammonia solutions of the reactants (to initiate reaction), was entirely vacuum jacketed, provided for temperature control through pressure control by an attached manostat, and was attached to a gas buret for collection of gaseous products. Liquid samples from the ammonia solutions, removed through the double wall reaction vessel, were quenched and analyzed in the manner of Krapcho and Bothner-By.⁵

(7) H. L. Dryden, Jr., G. M. Webber, and J. A. Cella, *J. Org. Chem.*, **26**, 3237 (1961).

(8) J. F. Eastham and D. R. Larkin, *J. Am. Chem. Soc.*, **81**, 3652 (1959).

(9) J. F. Eastham, C. W. Keenan, and H. V. Secor, *ibid.*, **81**, 6523 (1959).

(10) When benzene, lithium, and alcohol were mixed in stoichiometric ratio (1:2:2) and there was no lithium ethoxide initially present, only 12% of the metal went to form hydrogen,⁹ but since most of this evolution (eq. 2) occurred during the first portion of reduction (eq. 1), its effect on metal and alcohol concentrations throughout the reduction cannot be ignored. However, the presence of significant initial lithium ethoxide so retards evolution 2 as to obviate it as competitor to the reduction.

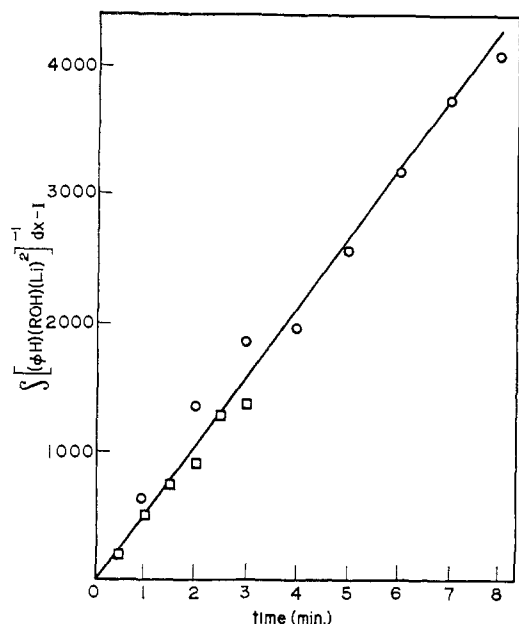


Figure 1. Fourth-order plot of two reduction runs (eq. 1) at -34° in ammonia containing initially *ca.* 0.15 *M* LiOEt: O, reactant concentrations initially in stoichiometric ratio; □, same except initial Li concentration doubled.

mental kinetic attributes of reduction 1 are revealed by our data: the rate of this reaction is profoundly affected by the concentration of a product, lithium ethoxide, and the rate law is fourth order in reactants, not third.

Plotted in Figure 1 are kinetic data for runs involving reaction solutions which were initially saturated with lithium ethoxide (*ca.* 0.15 *M*); the final points plotted for each run represent about 80% reaction. The two are plotted as fourth-order integrals vs. time so that if the reaction is first order each in alcohol and benzene and second order in lithium, coincidental plots of slope k_4 (eq. 3) should result. In one of the depicted runs the three reactants were in stoichiometric ratio (*ca.* 0.07, 0.14, and 0.14 *M*, respectively) while in the other the lithium concentration was doubled. The k_4 value calculated (linear least-squares slope) from the former run is 8.2 ± 0.4 , and from the latter run, 8.0 ± 0.4 (concn.⁻³ sec.⁻¹). Data from these two runs plotted as third order-integrals are not coincidental, nor do they show the same slope.

$$-d(\text{C}_6\text{H}_6)/dt = k_4(\text{C}_6\text{H}_6)(\text{EtOH})(\text{Li})^2 \quad (3)$$

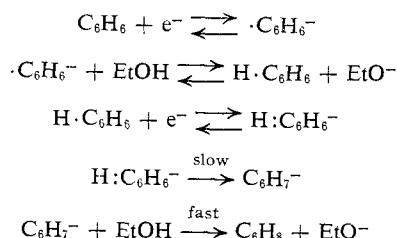
Satisfactory linear fourth-order plots (average $k_4 = 8.0$) were obtained from eight runs involving other variations in the concentrations of reactants (in the range *ca.* 0.03–0.3 *M*), in which the concentration of a product, lithium ethoxide, was initially sufficient for saturation. From runs with less or no initial lithium

Table I

Initial rate constant, k_4	LiOEt added, ^a <i>M</i>
71.2 ± 1.7	0.0
17.0 ± 1.9	0.05
8.2 ± 0.4	0.15 ^b
7.8 ± 0.3	0.60 ^c

^a Sufficient initial LiOEt to give this concentration if all were in solution. ^b Solution initially slightly turbid. ^c Considerable obvious precipitate.

ethoxide, much higher rate constants were apparent from initial slopes of fourth-order plots; deviation from linearity of these plots was also apparent, due both to buildup of ethoxide and to formation of some hydrogen before significant ethoxide was present.¹⁰ The effect of this base on the rate constant is shown in Table I. This effect and fourth-order kinetics can obviously be rationalized with hypothesis B above; indeed, it would seem inconsistent with fourth-order kinetics if there were no effect by base. The details of mechanism we will discuss subsequently.¹¹



Thus we conclude that the frequently cited^{13b-d,12a-d} statement that the rate “of metal-ammonia-alcohol reduction of benzene and some substituted benzenes . . . is governed by the law $d(\text{ArH})/dt = k(\text{ArH})(\text{M})\cdot(\text{ROH})^{1/3}$ ” is in error, at least in being too general. We wish to emphasize that the new findings reported here concern just the system in eq. 1. Currently we are studying other systems, *e.g.*, the use of *t*-butyl alcohol as proton source.^{12c}

(11) Briefly, by hypothesis B, as outlined below, after reversible addition of the first electron protonation occurs in an equilibrium. Increasing ethoxide (until saturation) would obviously so influence this equilibrium as to decrease the over-all reaction rate. We suggest that addition of the second electron could also involve an equilibrium and that the intermediate ($\text{H}:\text{C}_6\text{H}_6^-$) at that stage of reduction is a π -complex. The complex rearranges in a rate-determining step to the cyclohexadienyl anion (C_6H_7^-), which is rapidly protonated to product (C_6H_8).

(12) (a) W. L. Jolly in “Solvated Electron,” *Advances in Chemistry Series, No. 50*, American Chemical Society, Washington, D. C., 1965, pp. 27–35; (b) A. P. Krapcho and M. E. Nadel, *J. Am. Chem. Soc.*, **86**, 1096 (1964); (c) A. P. Krapcho and A. A. Bothner-By, *ibid.*, **82**, 751 (1960); (d) H. E. Zimmerman, *Tetrahedron*, **16**, 169 (1961).

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1,3,4-Oxadiazole

Sir:

The first of four possible isomeric unsubstituted oxadiazoles A–D was reported by the Belgian workers,¹



who made the thermally unstable 1,2,4-oxadiazole (A). Recently, Olofson and Michelman² prepared the thermally stable 1,2,5-oxadiazole parent nucleus B. We wish to record the preparation of the thermally stable 1,3,4-oxadiazole (C), the only isomer not containing an oxygen–nitrogen bond.

(1) C. Moussebois, R. Lenaers, and F. Eloy, *Helv. Chim. Acta*, **45**, 446 (1962).

(2) R. A. Olofson and J. S. Michelman, *J. Org. Chem.*, **30**, 1854 (1965).