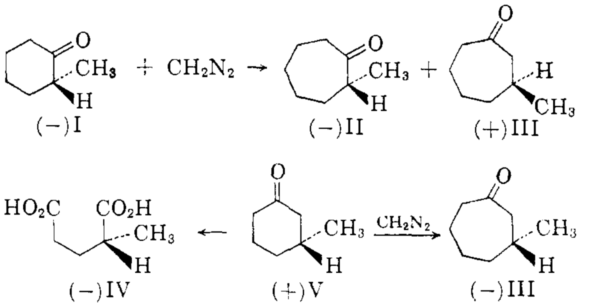
anone is established as (−) I, a conclusion also reached by Djerassi and co-workers.[4] The (−)-2-methylcycloheptanone (II) obtained from the ring enlargement of (−)-2-methylcyclohexanone should retain the absolute configuration of the starting ketone. In this connection it is interesting to note that although the sign of rotation and Cotton effect change in going from the cyclohexanone to cycloheptanone in the 3-substituted series,[5] this is not the case in the 2-substituted series.

If the configurational assignments to (−)-*α*-methylglutaric acid and the series of compounds which have been related to it are correct, and if the octant rule accurately predicts the configuration of 2-methylcyclohexanones, the inexorable conclusion is that the diazomethane ring enlargement of I to III proceeds with inversion of configuration. This seems inadmissible, however, on the basis of the generally-accepted mechanism which puts it in the class of nucleophilic 1,2-rearrangements (which in all known cases proceed with retention of configuration of the migrating group[8]), on the basis of other published observations (*e.g.*, diazomethane ring enlargement of *cis*-*α*-decalone yields *cis*-*β*-hexahydrobenzosuberone[9]), and in view of the fact that the ring enlargement of I *via* the Demjanow-Tiffeneau method (conversion of the ketone to the cyanohydrin, reduction of the cyanohydrin to the amino alcohol, and treatment of the amino alcohol with nitrous acid) follows the same steric course; *e.g.*, 2-methylcyclohexanone with $[\alpha]^{25}\text{D}$ +5.5° yielded 2-methylcycloheptanone with $[\alpha]^{25}\text{D}$ +29° and 3-methylcycloheptanone with $[\alpha]^{25}\text{D}$ −27°. It is hoped that experiments directed to the establishment of the absolute configuration of the 2-methylcyclohexanones by chemical interrelations will provide an answer to these contradictions.



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[8] D. J. Cram, "Steric Effects in Organic Chemistry," ed. by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 249.

[9] C. D. Gutshe and H. H. Peter, *J. Am. Chem. Soc.*, **77**, 5971 (1955).

A REVISED MODEL FOR AMMONIA SOLUTIONS OF ALKALI METALS

Sir:

It is well established that, in extremely dilute solutions of alkali metals in liquid ammonia, the metal is completely dissociated into ammoniated metal ions and ammoniated electrons. Each ammoniated electron is believed to exist in a large spherical cavity in the solvent and to be stabilized by the orientation of the ammonia dipoles on the periphery of the cavity. The decrease in the equivalent electrical conductance of these solutions as the concentration is increased to about 0.05 *M* indicates that ion pairing or assembly into larger aggregates takes place. The decrease of the molar paramagnetic susceptibility of the solutions with increasing concentration indicates that the ammoniated electrons associate to form species containing electron pairs. Both of these effects may be reproduced by assuming appropriate constants for these equilibria

$$M^+ + e^- = M$$

$$2M^+ + 2e^- = M_2$$

At −33° these equilibria shift in the vicinity of 0.01 *M* and the associated species predominate at higher concentrations.

It has been proposed by Becker, Lindquist, and Alder[1] that the monomer, M, consists of an ammoniated M^+ ion with the electron located in an expanded orbital on the protons of the coördinated ammonia molecules. Likewise, it has been proposed that the dimer, M_2, consists of two ammoniated M^+ ions held together by a pair of electrons in a bonding molecular orbital located principally between the two ions. These descriptions of the monomer and dimer are inconsistent with certain properties, in part newly measured, of alkali metal–ammonia solutions which are summarized below. We propose a revised description of the monomer and dimer species which more adequately accounts for all the properties of the solutions.

(1) The absorption spectra of sodium–ammonia solutions which are less concentrated than 0.03 *M* follow Beer's law within an experimental uncertainty of ± 2–5% at all wave lengths between 4000 and 25,000 Å. In fact, Beer's law is obeyed with similar precision for wave lengths between 4000 Å. and the absorption maximum (15,000 Å.) for concentrations at least as high as 0.1 *M*.[2] There is no indication of a separate absorption band near 6700 Å. Such a band has been observed in amines by Fowles, McGregor and Symons[3] and was attributed to a diamagnetic species. We have been unable to substantiate the claimed[4] appearance of shoulders at 6700 and 8000 Å. in the absorption spectra of ammonia solutions of sodium and sodium iodide. Thus the three species e^-, Na, and Na_2 have almost identical absorption spectra.

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[1] E. Becker, R. H. Lindquist and B. J. Alder, *J. Chem. Phys.*, **25**, 971 (1956).

[2] M. Gold and W. L. Jolly, unpublished data.

[3] G. W. A. Fowles, W. R. McGregor and M. C. R. Symons, *J. Chem. Soc.*, 3329 (1957).

[4] H. C. Clark, A. Horsfield and M. C. R. Symons, *ibid.*, 2478 (1959).

(2) The absorption spectra of solutions of lithium, potassium[5] and cesium are identical with those for sodium solutions of similar concentration within the limits of experimental uncertainty, which for the former solutions was ± 10%. Hence the spectra of the M and M_2 species (in the visible and infrared) do not depend upon the particular metal.

(3) Gunn and Green[7] have found that the apparent molar volume of lithium in ammonia 0° is practically constant at 50 ml./mole from 0.02 to 0.99 *M*. For sodium, the apparent molar volume changes only from 56.3 to 58.6 ml./mole from 0.0093 to 0.34 *M*. The latter data are inconsistent with some preliminary data of Evers and Filbert[8] which indicate a marked minimum in the volume–concentration curve for sodium at 0.03 *M*. However, until the latter findings are confirmed, we shall favor the former data and therefore conclude that the partial molal volumes of $M^+ + e^-$, of M, and of $^1/_2$ M_2 are nearly the same.

(4) Nuclear magnetic resonance data[9] are available only above 0.05 *M*. In the range 0.05 to 0.2 *M* the unpaired electron spin density on the sodium nuclei is only about 0.1% of that expected for isolated sodium atoms. The n.m.r. shift for nitrogen is rather large and indicates that an appreciable fraction of the unpaired electron spin density extends into the ammonia solvent regions. Since in this concentration range the concentration ratio of M to e^- is not small, the electron spin density on the metal atom nucleus must be small for the species M.

This evidence, taken as a whole,[10] is quite inconsistent with the Becker, *et al.*, model where the volumetric and spectral properties of ($e^- + M^+$), M, and $^1/_2$ M_2 would be expected to differ widely. Douthit and Dye[6] and Evers[11] have pointed out that if the monomer were simply an ion-pair consisting of an ammoniated metal ion and an ammoniated electron, the constancy of the spectra in the dilute range could be explained. They make no such proposal for the dimer. However, our spectral data require a new picture for M_2 as well. We picture the M_2 species as a quadrupolar ionic assembly of $2e^- + 2M^+$ in which there is little distortion of either the ammoniated electrons or ammoniated metal ions. Presumably the electrons and ions are held in a square or rhombic configuration. The probability density for the electron in the solvated e^- species extends with decreasing intensity through several solvent layers.[12] Thus the wave functions for the two e^- in M_2 will overlap significantly and it is reasonable that the singlet state should be lower in energy than the triplet by more than kT. Also a small electron density at the sodium nucleus in the ion pair (M) species is to be expected. Both the volume and the 1s–2p spectral frequency depend primarily on the cavity size for the solvated electron. Thus, if this cavity retains its size through ion pair and quadruplet formation, the results cited in (1), (2), and (3) above become understandable.

Presumably the solvated electron retains its structure in further polymeric species (*e.g.*, M_4) which probably form in more concentrated solutions. However, in highly concentrated solutions, one should expect that the nature of the ammoniated electrons would change if for no other reason than that there are insufficient ammonia molecules to properly coördinate both the metal ions and the electrons. We believe the deviations from Beer's law which occur in sodium solutions more concentrated than 0.03 *M* indicate the formation of high polymers with incipient metallic bonding.

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[5] We find no evidence for a negative deviation from Beer's law for potassium as reported by Douthit and Dye.[6]

[6] R. C. Douthit and J. L. Dye, *J. Am. Chem. Soc.*, **82**, 4472 (1960).

[7] S. R. Gunn and L. G. Green, *J. Chem. Phys.*, **36**, 363 (1962).

[8] E. C. Evers and A. M. Filbert, *J. Am. Chem. Soc.*, **83**, 3337 (1961).

[9] H. M. McConnell and C. H. Holm, *J. Chem. Phys.*, **26**, 1517 (1957); J. Acrivos and K. S. Pitzer, unpublished data.

[10] W. E. Blumberg and T. P. Das (*J. Chem. Phys.*, **30**, 251 (1959)) treat the n.m.r. data on the basis of the Becker, *et al.*, model with reasonable agreement. The fit is strained, however, and would be easier on our model.

[11] E. C. Evers, *J. Chem. Ed.*, **38**, 590 (1961).

[12] J. Jortner, *J. Chem. Phys.*, **30**, 839 (1959).

SECONDARY STRUCTURE AND AGGREGATION IN DEOXYGUANOSINE OLIGONUCLEOTIDES

Sir:

Recently the synthesis of deoxyguanosine oligonucleotides bearing 5′-phosphomonoester end groups has been accomplished in this laboratory.[1] Several properties, for example, resistance to venom phosphodiesterase, pointed to secondary structure in these compounds. This communication summarizes results of further studies which show that these oligonucleotides are capable of forming aggregates containing highly ordered polymeric structures. Examination of corresponding oligonucleotides of other deoxyribonucleosides[2] (thymidine, deoxyadenosine, deoxycytidine) under comparable conditions so far has failed to reveal this property in them.

Figure 1 shows the ultraviolet absorption increases in *d*-pGpGpG as a function of temperature. Thus, in 0.25 *M* phosphate buffer (Curve 1) the structure derived from this trinucleotide displays a T_m of about 58°. On keeping the heated solution at room temperature for two weeks the original structure is partially regained (Curve 2). In succinate buffer (0.25 *M*) the behavior is again typical of the collapse of an ordered structure but the T_m is much lower (28°) for an as yet unknown reason. Denaturation of the aggregate also may be accomplished by brief treatment with sodium hydroxide (0.1 *M*) at room temperature. The resulting solution on being kept in 0.25 *M* phosphate buffer for two weeks again displays a T_m of

[1] R. K. Ralph, W. J. Connors, H. Schaller and H. G. Khorana, paper in preparation.

[2] H. G. Khorana and J. P. Vizsolyi, *J. Am. Chem. Soc.*, **83**, 675 (1961); H. G. Khorana, A. F. Turner and J. P. Vizsolyi, *ibid.*, **83**, 686 (1961); R. K. Ralph and H. G. Khorana, *ibid.*, **83**, 2926 (1961).