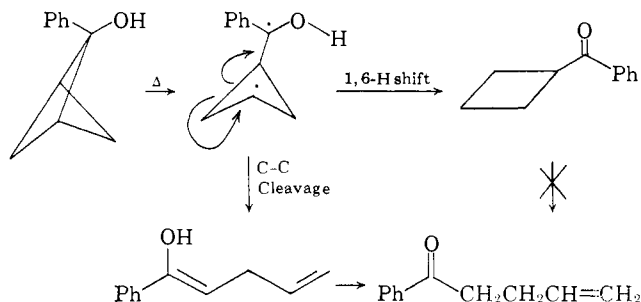
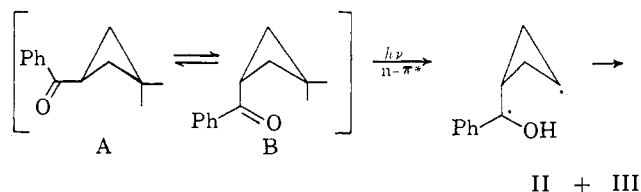


behavior of certain other organic compounds on electron impact and on pyrolysis,¹³ we were encouraged to investigate the pyrolysis of III. Thermolysis is readily effected in a heated injector unit of a F & M gas chromatograph and afforded a mixture of I and II (2:1 at 260°), presumably by the mechanism shown below.



Cyclobutylphenylcarbinol (IV) was identified by comparison of infrared and retention time with that of an authentic sample.¹⁴ The pinacol V, mp 131–133°, was found to be a mixture of *dl* and *meso* forms by nmr analysis. Lead tetraacetate cleavage of the pinacol V regenerated the reactant I, not only providing a structure proof but also a method for assaying pinacol. Further evidence for the structure of V was obtained by synthesis from I by reductive dimerization with aluminum amalgam–ethyl alcohol.

The most direct interpretation of our results involves a reaction of the $n-\pi^*$ triplet state as depicted in terms of the ensuing mechanism.



The cyclobutane ring is known to be puckered by about 30°, leading to both pseudo-axial and pseudo-equatorial positions which may be occupied by substituents.¹⁵ In one of the two possible conformations of I (conformer B), hydrogen abstraction by the $n-\pi^*$ excited state can proceed *via* a six-membered transition state. Once formed, the biradical intermediate undergoes spin inversion prior to ring closure (III) or elimination (II).¹⁶ The inefficiency of the photoprocess ($\phi_{III} = 0.004$) may be related to the low concentration of conformer B, thereby allowing for a high rate of internal decay. This interpretation is consistent with the formation of IV and V; both products are presumably derived by hydrogen abstraction from solvent by conformer A in its excited state. While irradiation of I in benzene afforded a mixture of products, photolysis in isopropyl alcohol afforded the pinacol as the virtually exclusive product ($\phi_V = 0.2$). Thus, the least stable conformation of I would be expected to undergo internal hydrogen ab-

(13) D. C. DeJongh, R. Y. Van Fossen, and C. F. Bourgeois, *Tetrahedron Letters*, 271 (1967).

(14) P. T. Lansbury and V. A. Pattison, *J. Am. Chem. Soc.*, **84**, 4295 (1962).

(15) J. B. Lambert and J. D. Roberts, *ibid.*, **87**, 3884 (1965).

(16) These processes may be considered to be analogous to the Norrish type II cleavage and cyclobutanol formation observed with the irradiation of aliphatic ketones containing γ -hydrogens.¹⁷

(17) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 154.

straction under conditions which suppress photoreduction of the more stable conformation. The photolysis could be quenched by the addition of naphthalene, in agreement with a $n-\pi^*$ triplet as the reactive excited state.

Several aspects of the solution and pyrolytic reactivity of substituted bicyclo[1.1.1]pentanes as well as the extension of the photosynthesis to related hetero systems are presently under active investigation in our laboratories.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant GP-6511).

Albert Padwa, Edward Alexander
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214
Received September 11, 1967

Spin Equilibrium in Tris(2-aminomethylpyridine)iron(II) Halides

Sir:

There is currently a large amount of interest in metal complexes near the "crossover" point.¹⁻⁷ The magnetic behavior of these complexes is seldom simple and usually does not follow closely that expected for a system with a ground state of a given spin multiplicity with a thermally accessible excited state of different multiplicity.^{1,2,6,8} The exact causes of the complications have not been established, but reasonable explanations have been proposed.^{1,2} A puzzling aspect to certain iron complexes is that the moment drops to some value well above that expected for a spin singlet and remains constant, at least down to 77°K.^{2,9} Another peculiarity that has been observed^{3,4,6} for some Co(II) complexes near the "crossover" point is that the magnetic behavior is markedly dependent upon the anion present, even when the anion is not coordinated to the metal.

We would like to present data which show that not only does the tris(2-aminomethylpyridine)iron(II) cation¹⁰ exhibit such a "spin equilibrium" but also that the different halide salts exhibit different magnetic behavior. Further, the moments show the previously mentioned peculiarity of dropping to a certain value and then remaining essentially constant down to 20°K. The magnetic moments for the Cl⁻, Br⁻, and I⁻ salts (analytical data are given in Table I) over the temperature range 20–300°K are shown in Figure 1.¹¹ Attempts to fit

(1) A. H. Ewald, R. L. Martin, J. G. Ross, and A. H. White, *Proc. Roy. Soc. (London)*, **A280**, 235 (1964).

(2) E. König and K. Madeja, *Inorg. Chem.*, **6**, 48 (1967).

(3) R. C. Stouffer, D. W. Smith, E. A. Clevenger, and T. E. Norris, *ibid.*, **5**, 1167 (1966).

(4) J. G. Schmidt, W. S. Brey, Jr., and R. C. Stouffer, *ibid.*, **6**, 268 (1967).

(5) J. P. Jesson and J. F. Weiher, *J. Chem. Phys.*, **46**, 1995 (1967).

(6) J. S. Judge and W. A. Baker, Jr., *Inorg. Chim. Acta*, **1**, 68 (1967).

(7) J. P. Jesson, S. Trofimenko, and D. R. Eaton, *J. Am. Chem. Soc.*, **89**, 3158 (1967).

(8) D. L. Williams, D. W. Smith, and R. C. Stouffer, *Inorg. Chem.*, **6**, 590 (1967).

(9) W. A. Baker, Jr., and H. M. Bobonich, *ibid.*, **3**, 1184 (1964).

(10) 2-Aminomethylpyridine is commonly called 2-picolyamine and is hereafter abbreviated 2-pic.

(11) The magnetic moments were calculated from the relationship $\mu_{\text{eff}} = 2.83(\chi_m T)^{1/2}$, where χ_m' is the molar susceptibility after correction for diamagnetism. The errors in the values of the moments are about ± 0.05 at the higher temperatures but increase to about ± 0.10 BM at the lower values.

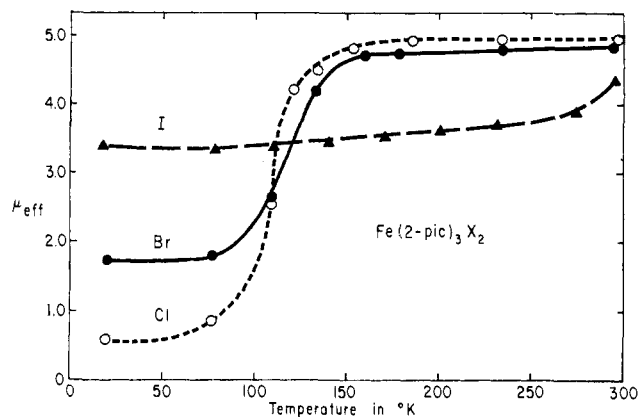


Figure 1. Plot of the magnetic moment (Bohr magnetons) vs. temperature.

these data to a model which involves a $^1A_{1g}$ ground state in thermal equilibrium with a $^6T_{2g}$ excited state, which is split into three levels by spin-orbit coupling, were futile. As was observed for some Co(II) systems,^{6,8} the data seem to suggest that the separation between states varies with temperature.

Table I. Analytical Data for the Tris(2-aminomethylpyridine)iron(II) Salts

Compound	Calcd, %			Found, %		
	C	H	Fe	C	H	Fe
[Fe(2-pic) ₃]Cl ₂	47.91	5.36	...	47.65	5.63	...
[Fe(2-pic) ₃]Br ₂	40.02	4.48	10.34	39.98	4.99	10.16
[Fe(2-pic) ₃]I ₂	34.09	3.81	...	34.16	3.64	...

In spite of the lack of quantitative agreement, the postulate of the simultaneous existence of two spin states is adequately supported by Mössbauer data. Such data have been obtained for the chloride and iodide salts. Because of absorption by bromine of the 13-Kev γ rays used in ^{57}Fe resonance studies, the bromide salt gave very poor spectra. For the chloride salt, the room temperature spectrum shows a pair of lines which are obviously a result of quadrupole splitting with an isomer shift of 0.98 and a splitting of 2.04 mm/sec.¹² These parameters are typical of high-spin iron(II).¹³ At 77°K, the spectrum shows two pairs of lines, an inner doublet with an isomer shift of 0.52 and a splitting of 0.55 mm/sec, and an outer doublet corresponding to the one seen at room temperature. The intensity of the inner doublet is about seven times that of the outer doublet, however. Further, the parameters of the inner doublet are about what are usually observed for low-spin iron(II).¹⁴ At 4.2°K, only the inner doublet is observed. For the iodide, the spectrum is not as well resolved as for the chloride, but it is clear that both the high-spin and low-spin components are observable at room temperature as well as at 77°K. Further, at liquid nitrogen temperature the relative intensities of

(12) Relative to natural iron foil.

(13) R. L. Collins, R. Pettit, and W. A. Baker, Jr., *J. Inorg. Nucl. Chem.*, **28**, 1010 (1966).

(14) The isomer shift is actually more positive than any we have seen in the literature for low-spin iron(II). This is perhaps to be expected since in this case the ligand field is as weak as it can be and still cause spin pairing, and, in general, the isomer shift decreases as the field increases.

the two components are about the same with the parameters being, within experimental error, the same as for the chloride. Thus the Mössbauer data agree almost perfectly with what would be predicted from the magnetic data.

Finally, we would like to mention that we have diluted the chloride salt with the corresponding zinc complex which from X-ray powder data is seen to be isomorphous with the iron complex. Magnetic and Mössbauer data for mixtures containing as little as 15% iron complex are identical, thus ruling out the possibility that the magnetic data could be explained by an antiferromagnetic interaction.

Acknowledgments. This work was supported by the National Science Foundation. We also thank Professor R. L. Collins of the University of Texas for obtaining the Mössbauer data at liquid helium temperature as well as confirming the data at other temperatures.

Gordon A. Renovitch, W. A. Baker, Jr.

Department of Chemistry, Syracuse University
Syracuse, New York 13210

Received September 1, 1967

Rates of Solvolysis of the *p*-Nitrobenzoates of the Tertiary 2-Methyl- and 3-Methyl-*cis*-bicyclo[3.3.0]octanols.

Evidence for Steric Hindrance to Ionization in the *endo* Derivatives

Sir:

In 1946 it was proposed that relief of steric strain accompanying the ionization of sterically crowded tertiary derivatives could provide a potent driving force to enhance the rate of solvolysis.¹ Today steric assistance to ionization is an accepted factor in calculating rates of solvolysis.²

In 1961 it was suggested that the *endo* derivatives of rigid bicyclics with U-shaped structures³ might undergo solvolysis with an increase in steric strain in the transition state, resulting in a decreased rate of solvolysis.^{4,5} However, this proposal for steric hindrance to ionization has not yet received serious consideration.^{6,7} Accordingly, we undertook to prepare and solvolyze suitable derivatives with representative U-shaped structures: bicyclo[3.3.0]octane, which the model suggests should provide smaller steric hindrance to ionization than norbornane, and *endo*-5,6-trimethylenenorbornane, which should exhibit larger.⁸

As was pointed out earlier, the use of secondary derivatives suffers from the disadvantage that the

(1) H. C. Brown, *Science*, **103**, 385 (1946).

(2) P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1854 (1964).

(3) It is convenient to extend the *exo,endo* terminology of norbornyl derivatives to the corresponding "outer" and "inner" derivatives of other U-shaped structures.

(4) H. C. Brown and S. Nishida, paper presented to the Division of Organic Chemistry at the 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961.

(5) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, pp 140-157, 176-178.

(6) S. Winstein, *J. Am. Chem. Soc.*, **87**, 381 (1965).

(7) However, see H. C. Brown, I. Rothberg, P. von R. Schleyer, M. M. Donaldson, and J. J. Harper, *Proc. Natl. Acad. Sci. U.S.A.*, **56**, 1653 (1966); P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Am. Chem. Soc.*, **87**, 375 (1965).

(8) The results with the latter system are reported in the following communication: H. C. Brown, I. Rothberg, and D. L. Vander Jagt, *J. Am. Chem. Soc.*, **89**, 6380 (1967).