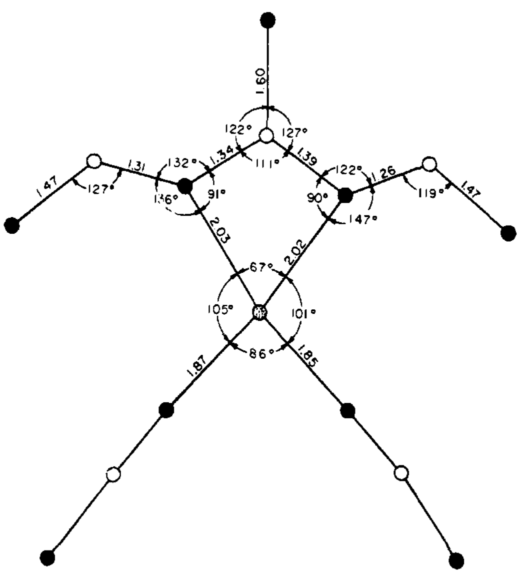
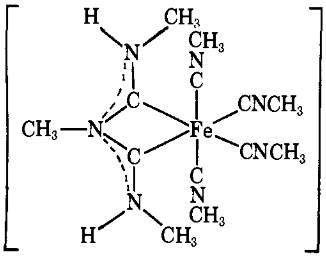


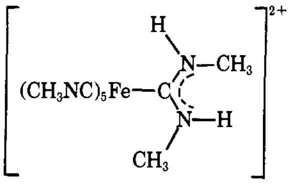
Figure 1. Distances and angles within the chelate ring of the (CH$_3$NC)$_4$Fe(C$_2$N$_3$(CH$_3$)$_3$H$_2$)$^{2+}$ ion: O, N; ●, C; ⊛, Fe. H atoms are not shown, and the two out-of-plane CH$_3$NC ligands have been omitted for clarity. Estimated standard deviations are 0.04 Å for Fe–C(chelate) and 0.05 Å for C–N. The average distances for the four isocyanide ligands are Fe–C, 1.86 (2), C–N, 1.15 (2), and N–CH$_3$, 1.48 (4) Å.

The spectrum consists of resonances at τ 6.92 (singlet (s), relative intensity 3), which is assigned to the internal methyl group of the chelate; 6.50 (s, 6), which is assigned to one of the pairs of equivalent unreacted isocyanide ligands; 6.50 (doublet, $J_{\text{H-N-CH}_3}$ = 5.0 Hz, 6), which is assigned to the terminal methyl groups of the chelate; 6.45 (s, 6), which is assigned to the second pair of equivalent unreacted isocyanide ligands; and a broad resonance at 1.62 (s, 2), which is assigned to the two nitrogen-bound protons. The coupling between the doublet at τ 6.50 and the broad resonance at τ 1.62 has been confirmed by double-resonance experiments.



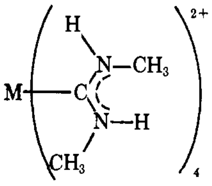
4

Presumably, the addition of methylamine to Fe(CNCH$_3$)$_6^{2+}$ to give **4** occurs stepwise *via* reaction **1**, with **5** formed as an intermediate. In **5**, a relatively



5

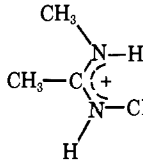
small isocyanide ligand has been converted into a bulky new ligand. In a six-coordinate complex, this ligand is forced close enough to the adjacent isocyanide groups so that a second addition reaction takes place to form **4**. The square-planar isocyanide complexes M(CNCH$_3$)$_4^{2+}$ (M = Pd, Pt) do not undergo chelative addition with methylamine, but instead add 4 mol of methylamine to yield **6**.[9] Molecular models show that **6** is sterically crowded and that the ligands must be



6, M = Pd, Pt

oriented so that the remaining coordination sites of the metal are effectively blocked. Therefore, multiple additions of this type are not likely for six-coordinate complexes.

The configurations adopted by the planar ligands in complexes such as **1–4** and **6** follow a common pattern which is related to the configuration of the *N*,*N*′-dimethylacetamidinium ion **7**. This ion adopts the amphi



7

configuration with one proton (a) and one methyl group (b) in the "inside" positions.[12] The configuration about each metal-bound carbon of the chelating ligand in **4** similarly has one proton and one methyl group in the inside positions. An X-ray study[7,8] of a derivative of **1** shows that the configuration about each metal-bound carbon of the chelate is such that one proton and one methyl group occupy inside positions. The ligands in **6**[9] and in some related complexes[6] also adopt amphi configurations.

Acknowledgment. This research was supported by Grants No. AM-14946 from the National Institutes of Health and GP-12299 from the National Science Foundation. We thank the University of Arizona Computer Center for computation time.

---

[12] G. S. Hammond and R. C. Neuman, Jr., *J. Phys. Chem.*, **67**, 1655, 1659 (1963).

Joel Miller, A. L. Balch*
Department of Chemistry, University of California
Davis, California 95616
John H. Enemark
Department of Chemistry, University of Arizona
Tucson, Arizona 85721

Received June 24, 1971

Effect of Ion-Pair Structure on Electron-Transfer and Proton-Transfer Equilibria

Sir:

The difference in electron affinities of acceptors[1,2] is the dominant factor determining the position of

---

[1] D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Amer. Chem. Soc.*, **78**, 116 (1956).

[2] J. Jagur-Grodzinski, M. Feld, S. L. Yang, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965).

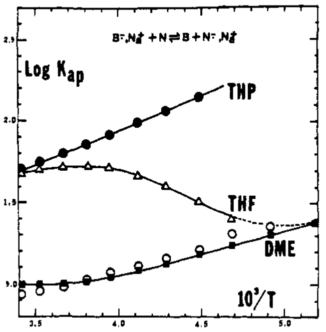


Figure 1. Electron-transfer equilibrium $B\cdot^-, Na^+ + N \rightleftarrows B + N\cdot^-,Na^+$; K_{app}' studied in THP, ●; THF, ▽; DME, ■; and THP + 10% tetraglyme, ○; ion-pair concentration $\sim 10^{-3}$ *M*. It was established that the addition of sodium tetraphenylboride to DME solution does not affect K_{app}', *i.e.*, even in this solvent in which the dissociation of ion pairs into free ions is most pronounced, the proportion of free ions is insignificant under conditions of our experiments.

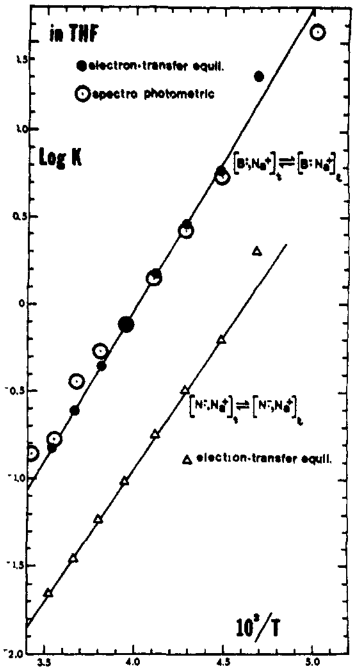


Figure 2. van't Hoff plot for the equilibria established in THF: $(B\cdot^-,Na^+)_{tight} \rightleftarrows (B\cdot^-,Na^+)_{loose}$; ●, from the electron-transfer equilibrium; ○, from the spectroscopic data; $(N\cdot^-,Na^+)_{tight} \rightleftarrows (N\cdot^-,Na^+)_{loose}$ from the electron-transfer equilibrium. $\Delta H_B = -7.9$ kcal/mol, $\Delta S_B = -32$ eu; $\Delta H_N = -6.9$ kcal/mol, $\Delta S_N = -32$ eu.

electron-transfer equilibria, *e.g.*

$$A_1\cdot^- + A_2 \rightleftarrows A_1 + A_2\cdot^- \qquad K_-$$

However, the state of aggregation of the ions or the structures of ion pairs also influence the respective equilibrium constants. For example, $K_\pm$ may differ from K_-,

$$A_1\cdot^-,Na^+ + A_2 \rightleftarrows A_1 + A_2\cdot^-,Na^+ \qquad K_\pm$$

their ratio being given by[3]

$$K_\pm/K_- = K_{diss,1}/K_{diss,2}$$

where $K_{diss,1}$ and $K_{diss,2}$ are the dissociation constants of the respective ion pairs.

We wish to consider a situation where two types of ion pairs, *e.g.*, tight and loose, coexist in a solution. In such a system two equilibria are established, *viz.*

$$(A_1\cdot^-,Cat^+)_{tight} + A_2 \rightleftarrows A_1 + (A_2\cdot^-,Cat^+)_{tight} \qquad K_{tight}$$

and

$$(A_1\cdot^-,Cat^+)_{loose} + A_2 \rightleftarrows A_1 + (A_2\cdot^-,Cat^+)_{loose} \qquad K_{loose}$$

The apparent equilibrium constant, K_{app}, determined spectrophotometrically and defined by

$$K_{app} = [A_1]\{[(A_2\cdot^-,Cat^+)_{tight}] + [(A_2\cdot^-,Cat^+)_{loose}]\}/[A_2]\{[(A_1\cdot^-,Cat^+)_{tight}] + [(A_1\cdot^-,Cat^+)_{loose}]\} \qquad (I)$$

is given then by

$$K_{app} = K_{tight}(1 + K_2)/(1 + K_1) = K_{loose}(1 + K_2^{-1})/(1 + K_1^{-1}) \qquad (II)$$

where K_1 and K_2 are the equilibrium constants of

$$(A_1\cdot^-,Cat^+)_{tight} \rightleftarrows (A_1\cdot^-,Cat^+)_{loose} \qquad K_1$$

and

$$(A_2\cdot^-,Cat^+)_{tight} \rightleftarrows (A_2\cdot^-,Cat^+)_{loose} \qquad K_2$$

Moreover

$$K_{tight}/K_{loose} = K_1/K_2 \qquad (III)$$

The temperature dependence of K_{app} may be most bizarre, *e.g.*, the van't Hoff plot of log K_{app} *vs.* $1/T$ obtained for the system sodium biphenylide $(B\cdot^-,Na^+)$, sodium naphthalenide $(N\cdot^-,Na^+)$ and their parent hydrocarbons B and N, respectively, shows a maximum (see Figure 1) when the reaction is investigated in tetrahydrofuran (THF). The values of K_{app}' were deter-

$$B\cdot^-,Na^+ + N \rightleftarrows B + N\cdot^-,Na^+ \text{ (THF)} \qquad K_{app}'$$

mined spectrophotometrically after acquiring detailed knowledge of the spectra and extinction coefficients of $B\cdot^-,Na^+$ and $N\cdot^-,Na^+$ in this solvent over the whole investigated temperature range.

The spectra and extinction coefficients of these ion pairs were also investigated in tetrahydropyrane (THP) and dimethoxyethane (DME) over a wide range of temperatures, and subsequently K_{app}' was determined in the latter two solvents. The results are included in Figure 1.

Let us now assume that for a given electron-transfer system K_{tight} and K_{loose} are *independent* of solvent, although K_1 and K_2 are profoundly affected by its nature. Examination of the spectra of $B\cdot^-,Na^+$ and $N\cdot^-,Na^+$ in THP and DME convinces us that only tight pairs exist in the former medium, and in the latter loose pairs only are present below $-30°$. However, both types of pairs coexist in THF, and the spectra indicate that the tight pairs dominate at 20° while the loose are the most abundant at the lowest temperatures. Thus, accepting our hypothesis, we obtain K_{tight} from studies of THP solutions and K_{loose} from investigation of the DME system. Therefore, we may calculate K_B and K_N for the THF system by solving the simultaneous equations (II and III), since K_{app} in THF and the ratio K_{tight}/K_{loose} are known.

$$(B\cdot^-,Na^+)_{tight} \rightleftarrows (B\cdot^-,Na^+)_{loose} \qquad K_B$$

$$(N\cdot^-,Na^+)_{tight} \rightleftarrows (N\cdot^-,Na^+)_{loose} \qquad K_N$$

---

(3) R. V. Slates and M. Szwarc, *J. Phys. Chem.*, **69**, 4124 (1965).

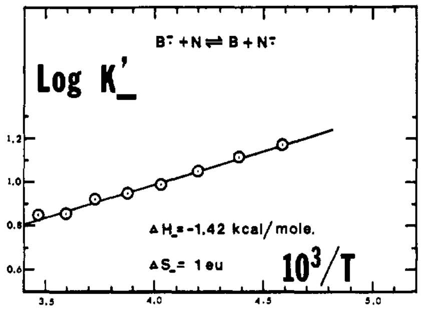


Figure 3. van't Hoff plot of the equilibrium involving free ions established in THF; $B\cdot^- + N \rightleftarrows N\cdot^- + B$; K_-.

The results are presented graphically in Figure 2 and give $\Delta H_B = -7.9$ kcal/mol, $\Delta S_B = -32$ eu and $\Delta H_N = -6.9$ kcal/mol, $\Delta S_N = -32$ eu.

Let us also assume that the spectra of tight and loose pairs are independent of solvent. Then K_B can be independently calculated from the spectra of $B\cdot^-,Na^+$ in THF, taking the spectra of $B\cdot^-,Na^+$ in THP and DME as those of pure tight and loose pairs, respectively. The results of such calculations are included in Figure 2 and show perfect agreement with those derived from the electron-transfer equilibrium data. Unfortunately, the complexity and overlap of the spectra of $N\cdot^-,Na^+$ prevent similar calculation of K_N from the spectroscopic data.

The validity of our hypothesis may also be checked by the following procedure. Addition of a small amount of a powerful solvating agent to a poor solvent converts the tight pairs into loose.[4–8] We examined, therefore, the equilibrium $B\cdot^-,Na^+ + N \rightleftarrows B + N\cdot^-,Na^+$ in THP and THF solutions containing 10% by volume of tetraglyme. The results agreed well with those obtained in DME, showing that indeed K_{loose} is *independent* of the solvent.

Equilibrium between the tight and loose $N\cdot^-,Na^+$ pairs in THF was studied by Hirota, *et al.*,[9] using esr techniques. His value $K_N = 4.8$ reported for −70° agrees well with ours, *viz.*, 4.5. However, his thermodynamic constants, $\Delta H_N = -5.6$ kcal/mol and $\Delta S_N = -24$ eu, differ somewhat from ours (see the caption of Figure 2). In a given solvent and for a given cation, ΔS values for the equilibrium tight pairs ⇄ loose pairs seem to be independent of the nature of the aromatic anion. Indeed, $\Delta S_B = -32$ eu, $\Delta S_N = -32$ eu (the present studies), and ΔS is again −33 eu for the analogous fluorenyl system.[4] Hirota's value, $\Delta S = -24$ eu, seems, therefore, too high.

The overall dissociation constants

$$(B\cdot^-,Na^+)_{\text{in whatever form}} \longrightarrow B\cdot^- + Na^+ \qquad K_{\text{diss},B\cdot^-,Na^+}$$

and

$$(N\cdot^-,Na^+)_{\text{in whatever form}} \longrightarrow N\cdot^- + Na^+ \qquad K_{\text{diss},N\cdot^-,Na^+}$$

in THF were determined[10] over a wide temperature range. Combining these data with $K_\pm$ shown in Figure 1, we calculate K_-

$$B\cdot^- + N \rightleftarrows N\cdot^- + B \qquad K_-$$

Although the van't Hoff plots for $K_{\text{diss},B\cdot^-,Na^+}$, $K_{\text{diss},N\cdot^-,Na^+}$, and $K_\pm$ are all curved (see ref 10 and Figure 1), a linear plot was obtained for K_-, as shown in Figure 3.

In conclusion, we have substantiated our hypothesis that the electron-transfer equilibrium for a given type of ion pair is independent of the solvent. We have also shown how the equilibrium constants for the conversion tight pair ⇄ loose pair may be calculated from studies of electron-transfer reactions. Finally, let us stress that the effect of ion aggregation or ion-pair structure on the proton-transfer equilibrium

$$A_1H + A_2^-,Cat^+ \rightleftarrows A_1^-,Cat^+ + A_2H$$

is the same as for the electron-transfer processes discussed in this communication. The mathematical and experimental approaches outlined here apply equally well to acid–base reactions. A fully documented account of this study will be published elsewhere.

Acknowledgment. Financial support of these investigations by the National Science Foundation is gratefully acknowledged.

Y. Karasawa, G. Levin, M. Szwarc*
Department of Chemistry
State University College of Forestry at Syracuse University
Syracuse, New York 13210

Received June 30, 1971

---

(4) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966).

(5) R. V. Slates and M. Szwarc, *ibid.*, **89**, 6043 (1967).

(6) (a) L. L. Chan and J. Smid, *ibid.*, **89**, 4547 (1967); (b) L. L. Chan, K. H. Wong, and J. Smid, *ibid.*, **92**, 1955 (1970).

(7) K. Höfelmann, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, **91**, 4645 (1969).

(8) L. Lee, R. Adams, J. Jagur-Grodzinski, and M. Szwarc, *ibid.*, **93**, 4149 (1971).

(9) N. Hirota, R. Corraway, and W. Schook, *ibid.*, **90**, 3611 (1968).

(10) P. Chang, R. V. Slates, and M. Szwarc, *J. Phys. Chem.*, 70, 3180 (1966).

Deuterium Isotope Effects on Thermal Cyclobutene Isomerizations. An Investigation of Competitive Conrotatory Ring Openings[1]

Sir:

There have been numerous reports of attempts to utilize secondary deuterium isotope effects to characterize the mechanism of cycloaddition reactions and related molecular isomerizations and rearrangements.[2] Although interpretation of these data has been the subject of some controversy, deuterium isotope effects have nevertheless often provided additional insights to subtle aspects of reaction mechanisms.[2,3]

Our interest in the cyclobutene–1,3-butadiene interconversion has led us to consider the utility of secondary deuterium isotope effects in describing further the mechanism of thermal isomerization of cyclobutenes.[4] In particular it was evident that a cyclobutene derivative having trans 3,4-dideuterio substitution (**1**) could undergo ring opening by two different conrotatory

---

(1) This communication comprises a portion of a dissertation submitted by M. L. Honig in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn, 1970.

(2) (a) T. J. Katz and R. Dessau, *J. Amer. Chem. Soc.*, **85**, 2172 (1963); also R. Dessau, Ph.D. Thesis, Columbia University, New York, N. Y., 1965; (b) P. Brown and R. C. Cookson, *Tetrahedron*, **21**, 1993 (1965); (c) R. J. Crawford and D. M. Cameron, *J. Amer. Chem. Soc.*, **88**, 2589 (1966); (d) W. R. Dolbier, Jr., and S. H. Dai, *ibid.*, **90**, 5028 (1968); (e) J. E. Baldwin and J. A. Kapecki, *ibid.*, **92**, 4874 (1970); (f) K. Humski, R. Malojčić, S. Borčić, and D. E. Sunko, *ibid.*, **92**, 6534 (1970).

(3) E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963).

(4) For recent reviews see H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 183 (1965); and R. Criegee, *Angew. Chem., Int. Ed. Engl.*, **7**, 559 (1968).