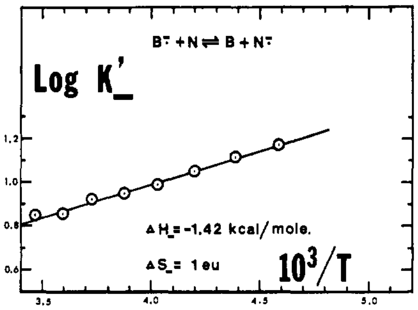

Figure 3. van't Hoff plot of the equilibrium involving free ions established in THF; $B\cdot^- + N \rightleftarrows N\cdot^- + B$; K_-.

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.

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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

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[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).

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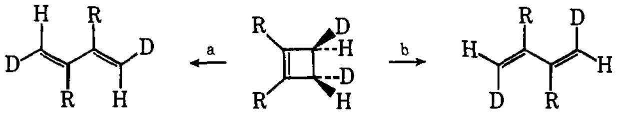
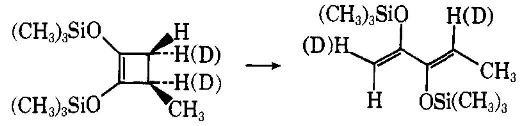
modes,[5] pathways a and b, respectively, distinguishable by the stereochemistry of the deuterium in the resultant 1,3-butadienes, **2a** and **2b**. Should these processes be kinetically differentiated, then a ratio of products (**2a**/**2b**) different from unity might be anticipated. In this communication we report observations bearing on this expectation.



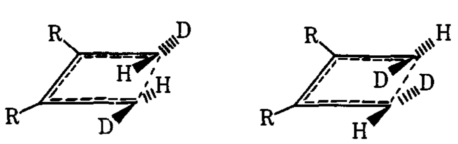
2a **1** **2b**

trans-3,4-Dideuterio-1,2-bis(trimethylsiloxy)cyclobutene (**1**) [R = $OSi(CH_3)_3$] and *cis*-3,4-dideuterio-1,2-bis(trimethylsiloxy)cyclobutene (**3**), stereospecifically deuterated derivatives of 1,2-bis(trimethylsiloxy)cyclobutene (**4**), were prepared from *dl*-dimethylsuccinate-d_2 and *meso*-dimethylsuccinate-d_2, respectively.[6,7] Isomerization of **1**, **3**, and **4** proceeded smoothly at *ca.* 180° ($t_{1/2}$ *ca.* 90 min)[8] and the product in each case was easily characterized as 2,3-bis(trimethylsiloxy)-1,3-butadiene by the nmr spectra; these exhibited besides a singlet at τ 9.90 (CH_3Si), two other well-separated and only slightly broadened singlets at 5.28 and 5.80 corresponding to the two different vinyl protons of the butadiene. Integration of these for products derived from **3** and **4** indicated a ratio indistinguishable from unity. In contrast, careful integration of the low-field singlets for the product obtained on isomerization of **1** gave an upfield-downfield ratio of 52.3:47.7,[9,10] revealing thereby an unequal proportion of **2a** and **2b** in this product.

To establish the identity of the predominant isomer in the mixture **2a** + **2b**, 3-methyl-1,2-bis(trimethylsiloxy)cyclobutene (**5**) and its cis 3,4-dideuterio derivative **6** were prepared starting with dimethyl pyrotartarate and *erythro*-dimethyl pyrotartarate-d_2, respectively.[6,7] It was expected that the direction of conrotatory ring opening of these cyclobutenes would be controlled by the C_3 methyl substituent[11] and that *trans*-2,3-bis(trimethylsiloxy)-1,3-pentadienes, **7** and **8**, would be formed stereospecifically. The stereochemistry of deuterium in diene **8** would thus be defined and nmr assignments could be made unambiguously. In fact, the vinyl proton region in the nmr of diene **7** consisted of singlets at τ 5.73 and 5.34 and a quartet ($J \sim 7.0$ Hz) at 4.60, whereas the nmr of diene **8** exhibited a singlet at 5.34.[12] Hence the high-field vinyl singlet in the nmr spectrum of **7** and **8** and by analogy the high-field singlet in the nmr spectrum of **2** [R = $OSi(CH_3)_3$] represents a proton cis to the trimethylsiloxy substituent, allowing therefore the conclusion that the predominant isomer formed on thermolysis of **1** [R = $OSi(CH_3)_3$] is the trans,trans d_2 isomer **2b** [R = $OSi(CH_3)_3$]. This conclusion is taken as evidence for selection between the two competitive conrotatory cyclobutene ring openings.[10] Considering further the importance of steric effects in such isomerizations,[4] our observations might best be explained in terms of the so-called "steric" deuterium isotope effect,[3,13] that is, as a consequence of the smaller effective size of carbon-bound deuterium compared with hydrogen. According to this view, the data thus reveal a preference for transition states involving deuterium–deuterium interaction over those involving hydrogen–hydrogen interaction (B *vs.* A). Simplified models of such processes suggest further that severe crowding will occur in nearly planar transition states *only* if the extent of C_3–C_4 bond cleavage is small and such transition states could thus be characterized as "closed." Evaluation of the kinetic secondary deuterium isotope effect for cyclobutene has led to a similar view,[14] although our study also shows a considerable variation in isotope effect (as might be expected) with C_3–C_4 disubstitution. A complete report of these results will be forthcoming.



5(**6**) **7**(**8**)



A B

Acknowledgment. Partial support of this research by the Research Corporation is gratefully acknowledged. We also recognize the generous support of the Department of Chemistry, Polytechnic Institute of Brooklyn.

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[8] J. J. Bloomfield, H. M. Frey, and J. Metcalfe have reported a study of the gas-phase thermal isomerization of 3 (*Int. J. Chem. Kinet.*, **3**, 85 (1971)). We wish to thank the authors for making their manuscript available to us prior to publication.

[9] Integration by planimetry; standard deviation less than ±0.5%. Similar ratios were evident after *ca.* 30% isomerization of **1** as well as after prolonged heating of the diene mixture (**2a** + **2b**).

[10] Although appropriate rate data for the formation of **2a** + **2b** were not obtained, a kinetic effect appears most probable.

[11] For instance, 3-methylcyclobutene gives only *trans*-1,3-pentadiene on isomerization: E. Gil-Av and J. Shabtai, *J. Org. Chem.*, **29**, 257 (1964).

[12] Actually, the intensity of the quartet at τ 4.60 and singlet at 5.73 was 30–70% of that expected, depending on the extent of deuterium incorporation.

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Novel Aryl Cyclic Sulfonium Zwitterions that Polymerize when Heated

Sir:

We wish to report a new class of zwitterion compounds in which the positive and negative sites are