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# Conformational effect in the stannous chloride debromination of *sym*-tetrabromoethane

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*Dedicated to Professor A. N. Campbell of the University of Manitoba*

The initial ratios of *cis*- to *trans*-dibromoethene product in the stannous chloride reduction of *sym*-tetrabromoethane in dimethylformamide were 1.51 ± 0.04 at 25°, 1.36 ± 0.03 at 50°, and 1.20 ± 0.03 at 75°. Transition state energy differences in the *trans–gauche* tetrabromoethane rotamers are estimated as $(H_t^{\ddagger} - H_g^{\ddagger}) = 480$ and $(F_t^{\ddagger} - F_g^{\ddagger}) = 244$ cal/mole at 25°. A conformational energy analysis was performed. We have shown how a rate-equilibrium parallelism can be adapted to a conformational analysis for systems of this type, and how $\alpha$, a constant between zero and unity, can be used to characterize the transition state relative to reactants and products (eq. [8]). In the present system, however, there is no rate-equilibrium parallelism and $\alpha$ cannot be defined.

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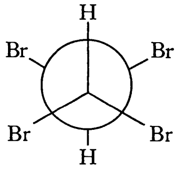
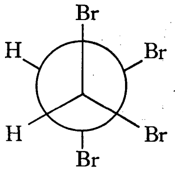
## INTRODUCTION

Conformational energy analyses of cyclohexane isomers are numerous and by now commonplace (1, Chap. 2). By comparison, acyclic systems have received scant attention (1, Chap. 1; 2). There is a semiquantitative study of the elimination reactions of the diastereoisomeric 1,2-diphenyl-1-propyl chlorides, bromides, and ammonium salts (3). There is a report (4) on the energetics of the zinc debromination of the rotamers of *sym*-tetrabromoethane, a heterogeneous reaction. In the present study, we investigated the conformational discrimination of a reductant, stannous chloride, toward the rotamers (I, II) of *sym*-tetrabromoethane in dimethylformamide (DMF).



*trans* (I)



*gauche* (II)

$$[1] \qquad C_2H_2Br_4 \xrightarrow[\text{DMF}]{\text{SnCl}_2} \textit{cis-}\text{ or }\textit{trans-}C_2H_2Br_2$$

## EXPERIMENTAL[2]

Anhydrous reagent grade stannous chloride was used; the effective stannous ion was 95.5%, determined iodometrically. Reagent grade lithium bromide was dried for 12 h at 120° and stored in a dessicator until required. The *sym*-tetrabromoethane, $n_D^{26.7}$ 1.6323, and the *cis*- and *trans*-dibromoethenes were prepared as reported previously (4). The solvent was anhydrous DMF, b.p. 62° (30 mm), $n_D^{25}$ 1.4270, purified by a standard method (6).

An Aerograph Model 90-P3 vapor phase chromatograph (v.p.c.) was used for product analysis. A column, 6 ft × 1/4 in., containing DEGS (diethylene glycol succinate) on Chromsorb "P" was kept at 99–100°. The retention times for *cis*- and *trans*-dibromoethene were 18.5 and 10.5 min, respectively, at a helium flow rate of 30 ml/min; no peak was obtained from our tetrabromoethane sample 6 h after its injection into the column. The *cis*/*trans* ratio was determined from the counts of a disc integrator: a known mixture, *cis*/*trans* = 1.15, was determined by v.p.c. as 1.13, with a precision of 1% for a duplicate determination.

Reaction [1] was carried out at three temperatures, 25 ± 2°, 50 ± 1°, and 75 ± 1°, so that the *cis*/*trans* product ratio could be determined. For reactions at 25 and 50°, tetrabromoethane (40 g) was dropped into stannous chloride (22 g, 2.0 *M*) in DMF (40 ml) solution. The total addition time was 10 min. For the 75° reaction, a stock solution of stannous chloride (50 g) in DMF (100 ml) was prepared and distributed into 10 ampules. Tetrabromoethane (10 ml) was added to each ampule and the ampules were sealed and immediately placed in the constant-temperature baths. The time for mixing and sealing was ca. 10 min. Our purpose in using such relatively high con-

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[2] Reference 5 contains further details.

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centrations was to obtain analyzable quantities of products in the shortest possible time and thus minimize possible changes in the product ratio.

Samples were removed from the reaction at intervals, poured into water, and extracted with ether. The ether solution was washed four times with water, dried with calcium chloride, and analyzed by v.p.c.

The possibility that *cis–trans* isomerization of the products might occur was checked by keeping the pure *cis*-dibromoethene at 50° for 200 min; no trace of *trans* could be found.

A blank run with a known mixture of *cis*- and *trans*-dibromoethene (*cis*/*trans* = 1.47) and stannous chloride in DMF was run at 50°. For our system, the change in the product ratio (time, in min) was insignificant: 1.47 (0), 1.49 (10), 1.46 (30), 1.48 (130), 1.49 (250). However, when lithium bromide (3 g, 0.59 *M*) was added to a standard reaction mixture at 50°, the *cis*/*trans* product ratio decreased with time. These and other observed ratios are displayed in Fig. 1.

## RESULTS AND DISCUSSION

Initially, we anticipated no difficulties in determining the *cis*/*trans* product ratio in reaction [1] (4). However, this ratio did fall with time, and it became apparent that we required the ratio at zero reaction time. Clearly, the ratio could decrease because of reactions which produce more *trans*- or consume more *cis*-dibromoethene. Our blank experiments appear to rule out *cis* to *trans* isomerization but implicate a process involving bromide ion. As the reaction proceeds, bromide ion is formed, and the proportion of *cis* decreases. Secondly, added bromide ion reduces the zero time *cis*/*trans* ratio from 1.36 to ca. 1.15. Once we ascribe the falling ratio to a competing reaction of bromide ion with tetrabromoethane,[3] we can minimize this as a source of error by working at low conversions, when the bromide ion effect will be least.

An extrapolation of our results in Fig. 1 to zero time yields *cis*/*trans* ratios of 1.51 ± 0.04 at 25°, 1.36 ± 0.03 at 50°, and 1.20 ± 0.03 at 75°. An Arrhenius-type plot of these ratios is given in Fig. 2. From the slope of this plot, we calculated an enthalpy difference of 480 ± 50 cal/mole. As we shall see, this will be identified with $H_t^{\ddagger} - H_g^{\ddagger}$ or the difference in the enthalpies of the *trans* and *gauche* transition states.

For this system [1], the conformational energy analysis is straightforward (1, Chap. 1; 2; 4), provided that one makes the assumption that [1] is a *trans* stereospecific E2 process from the *trans* and *gauche*

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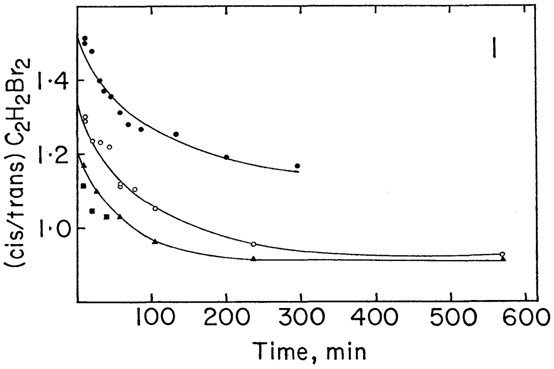
[3] Although bromide ion is ineffective as a debrominating agent in methanol (4), its halogen nucleophilicity increases markedly in DMF (ref. 5 contains further details).



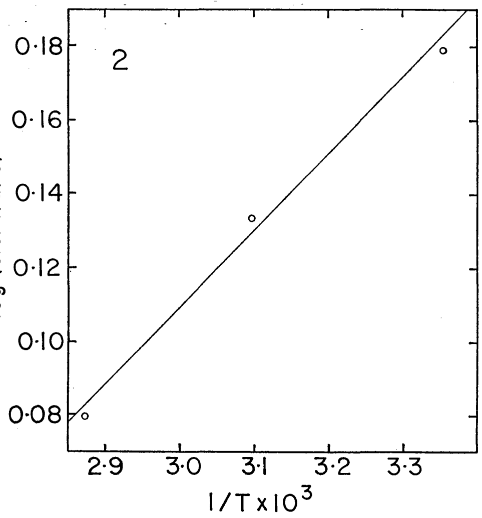


FIG. 1. Reaction between *sym*-tetrabromoethane (1.96 *M*) and stannous chloride (2.0 *M*) in DMF: (●) 25°, (○) 50°, (▲) 75°. Product ratios at 50° with added LiBr (0.59 *M*) are indicated by (■).

FIG. 2. The dibromoethylene ratio for the reaction of *sym*-tetrabromoethane and stannous chloride in DMF.

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rotamers of tetrabromoethane (7; 8, p. 209ff.; 9; 10).

$$trans\text{-}C_2H_2Br_4 \xrightarrow{SnCl_2} trans\text{-}C_2H_2Br_2$$

$$gauche\text{-}C_2H_2Br_4 \xrightarrow{SnCl_2} cis\text{-}C_2H_2Br_2$$

Admittedly, this basic assumption is only reasonable and plausible, but it is based on the many cases of *trans* stereospecific eliminations of bromine from *aliphatic acyclic* 1,2-disubstituted-1,2-dibromoalkanes by iodide, zinc, or lithium aluminium hydride (7; 8, p. 209ff.; 9; 10). *sym*-Tetrabromoethane is such an alkane (11); moreover, stannous ion is a two-electron reductant analogous to those just mentioned. We recognize that other mechanisms must be invoked for other dibromides, e.g. of stilbene (ref. 5 contains further details) (10, 12) or ethylene (8, p. 209ff.; 9), and for other reductants, e.g. sodium (7, 12). Since conformational equilibrium is maintained (rotation is rapid on the time scale of the elimination process) we write $K = [t]/[g]$. The reaction velocity expressions for each rotamer are combined (4):

$$[2] \quad \nu_t/\nu_g = k_t[t]/k_g[g] = (k_t/k_g)K.$$

The relative rate of formation, $\nu_g/\nu_t$, is clearly equivalent to the *cis*/*trans* product ratio we have determined. Since the free energy of activation is defined as

$$\Delta F^{\ddagger} = F^{\ddagger}(\text{transition state}) - F(\text{ground state}),$$

we can write

$$[3] \quad (F_t^{\ddagger} - F_g^{\ddagger}) = (\Delta F_t^{\ddagger} - \Delta F_g^{\ddagger}) + (F_t - F_g).$$

Similarly,

$$[4] \quad (H_t^{\ddagger} - H_g^{\ddagger}) = (\Delta H_t^{\ddagger} - \Delta H_g^{\ddagger}) + (H_t - H_g).$$

Since the right-hand sides of eqs. [2] and [3] are interconvertible,

$$[5] \quad (F_t^{\ddagger} - F_g^{\ddagger}) = -2.303\, RT \log \nu_t/\nu_g.$$

It should be noted that statistical factors of two, which arise from the two *gauche* forms, as well as the two modes of *trans* elimination from the *trans*-tetrabromoethane, cancel in the preceding expression [5].

The interconversion of the rotamers of liquid tetrabromoethane has been examined by several groups. For process [6],

$$[6] \quad gauche\text{-}Br_2CHCHBr_2 \rightleftharpoons trans\text{-}Br_2CHCHBr_2,$$

the first value for $(H_t - H_g) = 9.10 \pm 50$ (13) has been altered to 750 cal/mole (R. E. Kagarise, cited in ref. 14), and $\Delta S = -1.5$ e.u. (entropy units) has been calculated (14).[4] Moreover, the solvent change from liquid tetrabromoethane (dielectric constant = 7.0 at 22° (17)) to DMF (dielectric constant = 37.6 at 25° (18)) should not increase $(H_t - H_g)$ significantly $< 10\%$ (19). Taking note of these uncertainties, we can proceed to apply eqs. [3] and [4]; the results are given in Table I. Because of the revised values of the thermochemical quantities now available for [6], an analysis of the data for the zinc debromination of tetrabromoethane is also included.

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[4] Values of $H_t - H_g$ of 900 and 0 or ∞ cal/mole have also been given by Lamb (15) and Miyagawa (16).

TABLE I

Conformational energy analysis of the debromination of *sym*-tetrabromoethane, in cal/mole

| System | $T$ (°C) | $(F_t - F_g)$ | $(F_t^{\ddagger} - F_g^{\ddagger})$ | $(\Delta F_t^{\ddagger} - \Delta F_g^{\ddagger})$ | $(F_{trans} - F_{cis})$ |
|---|---|---|---|---|---|
| $SnCl_2$, DMF | 25 | 1 209±200 | 244±20 | −965±220 | 370±25 |
| | 50 | 1 247 | 197 | −1 050 | 365 |
| | 75 | 1 286 | 126 | −1 160 | 355 |
| Zn, $CH_3OH$* | 25 | 1 209 | 240 | −966 | 370 |
| | 64.5 | 1 270 | 160 | −1 110 | 360 |

| System | | $(H_t - H_g)$ | $(H_t^{\ddagger} - H_g^{\ddagger})$ | $(\Delta H_t^{\ddagger} - \Delta H_g^{\ddagger})$ | $(H_{trans} - H_{cis})$ |
|---|---|---|---|---|---|
| $SnCl_2$, DMF | | 750±150 | 480±25 | −270±175 | 480±25 |
| Zn, $CH_3OH$* | | 750 | 810±300 | 60±450 | 480 |

*Data from ref. 4.

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For comparison, we shall require equilibrium data on the products. Reasonable estimates for process [7],

$$[7] \qquad cis\text{-}C_2H_2Br_2 \rightleftharpoons trans\text{-}C_2H_2Br_2,$$

are $H_{trans} - H_{cis} \simeq 480$ and $F_{trans} - F_{cis} \simeq 360$ cal/mole in DMF at 25° (4).

In a process as important as elimination, it is of interest to characterize the transition state. One of the useful tenets here is that the energy increment between two reactants and their products changes monotonically. Graphically, this means that the energy difference for superimposed plots of the two profiles, i.e. of energy versus reaction coordinate, simply increases or decreases (8, p. 156ff.); analytically, we can cast the rate-equilibrium parallel in the form (20)

$$[8] \quad [F_t^{\ddagger} - F_g^{\ddagger}] = (1 - \alpha)(F_{trans} - F_{cis}) + \alpha(F_t - F_g).$$

As an extra-thermodynamic assumption, eq. [8] is not binding, but where it does apply, the constant $\alpha$ provides a numerical measure between zero and unity of the progress of reaction.

How are we to interpret the results of the energy analysis in Table I for the two debromination processes? One might first be tempted to characterize the transition states as "product-like", because of the rough similarity in $(F_t^{\ddagger} - F_g^{\ddagger})$ and $(F_{trans} - F_{cis})$. In the stannous chloride, but not the zinc debromination reaction, the similarity carries over to the enthalpy terms. For the "resemblance" to be valid, it should, of course, involve both enthalpy and free energy (or entropy) terms. The problem of comparison is exacerbated by the fact that $(H_t^{\ddagger} - H_g^{\ddagger})$ and $(F_t^{\ddagger} - F_g^{\ddagger})$ are *not* bracketed by the corresponding terms for reactants and products. The constant $\alpha$ of [8] is larger than unity and outside its allowed range. Clearly, estimates of the degree of bond breaking in the transition states cannot be based on energy criteria or on rate-equilibrium parallelism in *these* systems.

Let us recapitulate. Our conformational analysis began with the assumption that both rotamers were debrominated according to the same mechanism. The analysis could be carried through rigorously, subject to the usual uncertainties, e.g. in $(F_t - F_g)$. It was then apparent that the extra-thermodynamic assumption [8] was inapplicable. It is possible that the assumption of a single elimination mechanism for both isomers is invalid and [8] should not apply. In any case, the present results are somewhat unexpected and certainly not tidy; in view of the paucity of conformational analyses for such systems, our redox system will have to stand as something of a challenge.

## ACKNOWLEDGMENT

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