

Pressure Effects on the Rates of Aromatization of Hexamethyl(Dewar benzene) and Dewar Benzene. Volume as a Factor in Crowded Molecules^{1a}

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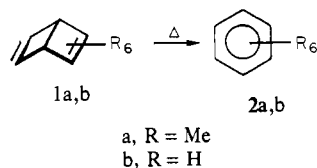
Abstract: The effect of pressure on the rate of aromatization of hexamethyl(Dewar benzene) (**1a**) has been remeasured, and that of the parent Dewar benzene (**1b**) has been determined for the first time. The results for the former reaction in bromobenzene at 140 °C indicate that the activation volume is $-(12 \pm 3)$ cm³/mol, and that for the latter in pyridine at 42.1 °C is $+(5 \pm 2)$ cm³/mol. This difference between the two reactions is attributed to the efficient packing of the methyl groups as they undergo gear engagement on the way to hexamethylbenzene (**2a**); the overall reaction volume in the reaction of **1a** is -22 cm³/mol. This conversion is also subject to an induced side reaction which is held responsible for an earlier overestimate of the volume reduction.

Introduction

Pressure effects on rate and equilibrium constants have become a popular tool in the investigation of reaction mechanisms in the past 20 years. Studies using this tool lead to quantitative information concerning the volume profile of the reaction of interest. Since the volume changes exhibited by a reacting molecule are obviously closely related to its structural changes, this information can often give a very direct insight into the detailed pathway followed by the reaction.² These correlations have become widely known, and many organic and inorganic chemists have made efforts to determine the pressure coefficient of their reactions. Several thousand reaction and activation volumes are now known, and virtually all the major reactions have been characterized with respect to the volume. The information so gathered has been organized in several reviews.³

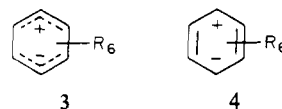
A basic tenet is that bonding—whether covalent or electrostatic—reduces the volume, and vice versa. This apparently simple rule has, of course, many facets, but striking agreement has been found in virtually all instances in which independent alternative information is also available. There are, however, a very few instances in which pressure effects have been reported that seem to be far from, or even opposite to, those that would be predicted on the basis of current alternative insights. In the past, further studies of those cases, in particular, have proved rewarding.⁴ In this paper, we report a study of one such apparent conflict; the accompanying paper describes another.

In 1974, Plieninger⁵ reported a high-pressure study of the aromatization of hexamethyl(Dewar benzene) (**1a**):



The volume of activation was found to be -35 cm³/mol,⁶ an

astonishing result indicating a major shrinkage of the reacting species along the reaction coordinate. It was furthermore found that the reaction volume was also negative, though by a smaller amount (-22 cm³/mol), so that the transition state appeared to represent a minimum in the volume profile. Apart from the size of the volume decrease, the very fact that shrinkage appeared to characterize the reaction at all intrigued us; no matter what the details may be, the 1,4 bond must break, and hence some expansion would be expected. It is well known⁷ that *heterolytic* cleavage producing ions virtually always reduces the volume (since the ions are solvated, i.e., electrostatically bound), but such a cleavage in the present case to give **3** or **4** seems intuitively unlikely, and it



is, in fact, ruled out on the experimental basis of solvent insensitivity.⁶ We therefore decided to investigate the reaction further, beginning with a redetermination of the volume profile of **1a**.

Results and Discussion

A careful check of the isomerization of **1a** turned up two aspects to which we can find no reference in the literature. One of these is that, although the reaction initially shows good first-order behavior, in the later stages it appears to become accelerated. That is to say, first-order plots show some upward curvature; this is true especially under pressure (see Figure 1). The effect is sometimes quite pronounced; thus, while the first-order plots are straight during the first half-life, the reaction was in some instances complete after the second "half-life" (**1a** no longer detectable). The second unexpected feature is exhibited by the ¹H NMR spectrum, which initially consists of the 2:1 singlets of the vinylic and allylic methyl groups at δ 1.6 and 1.1, respectively; in later stages it shows not only the sharp singlet of **2a** at δ 2.0 but also two broad signals δ 1.7 and 1.0, and also in a 2:1 ratio (Figure 2). The material producing these signals usually represented approximately 10% of the total product. Evidence of the side reaction was found with two samples of different origin.⁸

The isomerization appears to have an independent second mechanism which has an induction period, but which eventually becomes faster than the simple aromatization. Efforts to either induce this behavior by the addition of an initiator (benzoyl peroxide) or suppress it with a scavenger (hydroquinone) or base

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(8) We thank Professor H. Hogeveen for contributing one of these. The other was prepared at Stony Brook; see Experimental Section.

(1) (a) Presented as part of a plenary lecture at the Eighth AAPT Conference in Uppsala, Sweden, 1981 (by W. J. le Noble). (b) Stony Brook (c) Socorro.

(2) (a) N.S. Isaacs, "Liquid Phase High Pressure Chemistry", Wiley, New York, 1981; (b) W. J. le Noble and H. Kelm, *Angew. Chem., Int. Ed. Engl.*, **19**, 841 (1980); (c) "High Pressure Chemistry", H. Kelm, Ed., Reidel, Boston, Mass., 1978; (d) W. J. le Noble, *J. Chem. Educ.*, **44**, 729 (1967).

(3) (a) T. Asano and W. J. le Noble, *Chem. Rev.*, **78**, 407 (1978); (b) W. J. le Noble, *Prog. Phys. Org. Chem.*, **5**, 207 (1967); (c) G. A. Lawrance and D. Stranks, *Acc. Chem. Res.*, **12**, 403 (1979).

(4) See, for example, (a) W. J. le Noble, D. M. Chiou, and Y. Okaya, *J. Am. Chem. Soc.*, **101**, 3244 (1979); (b) W. J. le Noble and R. Mukhtar, *ibid.*, **97**, 5938 (1975); (c) W. J. le Noble and Y. S. Change, *ibid.*, **94**, 5402 (1972).

(5) H. Plieninger, H. P. Kraemer, and R. Mündnich, Abstracts, Fourth AAPT Conference, Kyoto, 1974, p 248.

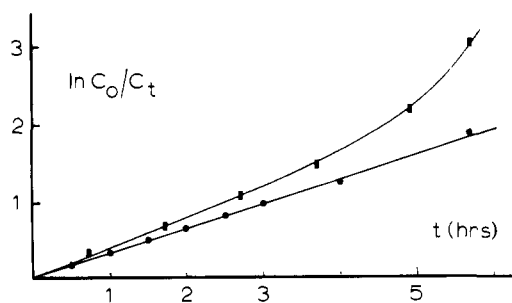


Figure 1. Typical first-order rate plots observed with **1a**. The circles represent data at atmospheric pressure; the rectangles are for the reaction at 69 MPa (both at 140 °C).

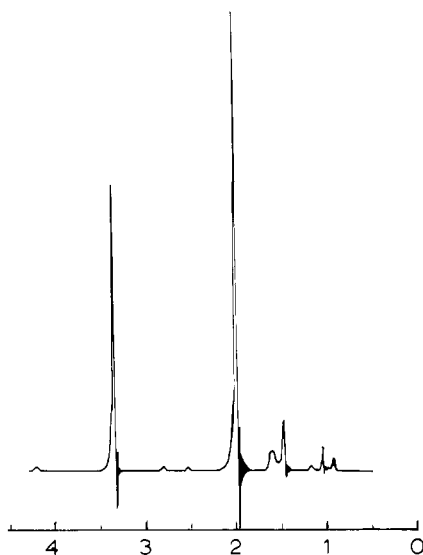


Figure 2. Methyl region of the ^1H NMR spectra typically observed late in the reaction of **1a**. From left to right are PhOCH_3 (internal standard) and $\text{C}_6(\text{CH}_3)_6$, each with a pair of ^{13}C satellites, and the two hexamethyl(Dewar benzene) peaks flanked by the unidentified product.

(pyridine) were essentially without effect. The absence or present of laboratory lighting also seemed to make no difference (a photochemical quantum chain mechanism is known⁹). We found in one instance that introducing some material of a finished reaction did reduce or remove the induction period for a fresh batch. So far as the unidentified product is concerned, the broad signals suggest a polymeric nature. Permeation gel chromatography showed the presence of several oligomers; however, we were not able to purify any of them. The chemical shifts point to a hexamethylbenzene polymer, but the only other support we can offer for this suggestion is that pyrolysis converts it largely into **2a**.

Our reason for describing these anomalies is that they are probably responsible for Plieninger's earlier result. The rather high pressure range used by his group (up to 1 GPa) virtually ensured that the delayed reaction and/or polymerization played a major role, and since covalent bond formation can be characterized by a volume contraction of as much as 20 cm^3/mol , the observation of a large and negative activation volume would be comprehensible on that basis.

If we now turn¹⁰ our attention to the initial part of the reaction, the evidence is that the fitting to first behavior then is altogether

Table I. Aromatization Rate Constants^a of **1a** and **1b**

substance	t , °C	p , MPa ^b	$10^5 k$, s ⁻¹
1a	120	0.1	0.9 ± 0.2
	120	138	1.8 ± 0.2
	140	0.1	4.5 ± 0.1
	140	69	5.0 ± 0.1
	140	138	6.3 ± 0.2
	145	0.1	8.8 ± 0.3
1b	42.1	4.2	2.9 ± 0.1
	42.1	55	2.6 ± 0.1
	42.1	104	2.4 ± 0.1
	42.1	215	2.4 ± 0.1

^a 5–12 points taken for each rate constant. ^b 1 MPa \approx 10 atm.

justified. No difference was found between two samples of different origin, and at atmospheric pressure—where the first-order plots were linear for periods longer than 2 half-lives—no difference was observable, whether separate samples were used to assay each kinetic point or whether a single solution was used for a whole run with periodic measurements. Restricting our attention then to this early part of reaction in which the first-order rate law clearly applies, we still find that the simple aromatization is accelerated by pressure, albeit by a factor much smaller than that reported;⁶ the activation volume is $-(12 \pm 3) \text{ cm}^3/\text{mol}$. In order to gain a complete picture of the volume profile of the reaction, we also measured the partial molar volumes of the reagent and its product; density measurements of bromobenzene solutions at 20 °C show that these volumes are 199 and 177 cm^3/mol , respectively. Thus, the reaction volume is $-22 \text{ cm}^3/\text{mol}$ as reported by Plieninger,⁶ but the transition state does not represent an extremum in the volume profile, and the molecule diminishes monotonically in size as it traverses the reaction coordinate.

We now attribute these results to the pronounced increase in crowding that must occur as the molecule approaches the planar structure, forcing the eclipse of all six of the methyl groups. The structure of the bicyclic valence isomer is known¹¹ from a study utilizing electron diffraction. The principal reported feature related to the present study is that **1a** has unusually long double bonds (1.35 Å), so that little volume change should accrue from the change in interaction between the neighboring pairs of vinylic methyls during reaction; however, four new methyl–methyl interactions are produced as the single bonds assume double-bond character and the dihedral angles vanish. The proximity of the methyls in the aromatic product may be gauged from the fact that force-field calculations by Iroff¹² led her to the conclusion that the substituents are subject to the gear effect; i.e., that their rotations are correlated. The result is expected to be a much more compact structure, and hence an increased density.

The effect of crowding on density is obviously most pronounced in hexasubstituted benzenes, but it is demonstrable even in the disubstituted ones. Inspecting tables of densities of substituted aromatic compound in the liquid state, one finds that ortho-disubstituted benzenes invariably have molar volumes 3–4 mL smaller than the meta- and para-substituted isomers. Since the isomerization at issue brings about four *additional* changes of skewed syn conformation, our observations seem reasonable.

This interpretation can be tested most simply by measurement of the volume profile of the aromatization of Dewar benzene itself. Since the methyl groups presumed to be responsible for the volume decrease are absent, the volume of reaction should be nearly zero and the activation volume should have the small positive value related to the lengthening of the 1,4 bond. The reaction volume was not measured because the amounts of parent dewar benzene that can be made by means of the van Tamelen synthesis are not of sufficient concentration for accurate dilatometry or density measurements, but the rates and hence the activation volume can be determined. The result—based on rate constants which are clearly first order throughout—is that in pyridine solution at 42.1

(9) (a) T. R. Evans, R. W. Wake, and M. M. Sifain, *Tetrahedron Lett.*, 701 (1973); (b) G. Jones and S.-H. Chiang, *J. Am. Chem. Soc.*, **101**, 7421 (1979). (c) For a more general discussion of the role of excited states in dewar benzene isomerizations, see N. J. Turro, J. McVey, V. Ramamurthy, and P. Lechtken, *Angew. Chem., Int. Ed. Engl.*, **18**, 572 (1979).

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$^{\circ}\text{C}$, $\Delta V^{\ddagger} = +(5 \pm 2) \text{ cm}^3/\text{mol}$ (Table I). This confirms our view of the hexamethyl analogue.

We take parenthetic note of the thermal activation parameters of **1a**, calculated from the data in Table I; they are: $\Delta H^{\ddagger} = 30 \pm 2 \text{ kcal/mol}$, and $\Delta S^{\ddagger} = -11 \pm 1 \text{ eu}$. Previous measurements of these parameters and the heat of reaction are suspect because the existence of the side reaction was not known. The reported values¹³ for **1b** are: $\Delta H^{\ddagger} = 23 \text{ kcal/mol}$, and $\Delta S^{\ddagger} = -5 \text{ eu}$. The relationship between the values for the two compounds is understandable on the basis of steric crowding in **1a** and in \ddagger transition state. It would appear from these data that the strain energy in the transition state for **1a** is approximately 7 kcal, and the lower entropy can be ascribed to steric interference with free rotation of the methyl groups. Although we can no longer trust the difference in measured enthalpies of reaction as a measure of strain energy in hexamethylbenzene, it can be estimated in a different way. A plot of $H_{f(g)}^{14}$ vs. carbon number is accurately linear in the series benzene, toluene, *m*-xylene, mesitylene, in which methyl groups do not interfere. The value for **2a**, however, is 6.7 kcal lower than the extrapolated value. Comparison with the difference in activation enthalpy indicates that most of the strain must already be present in the transition state.

In retrospect, our high-pressure results now seem less surprising than they did at first; perhaps, they should even have been anticipated. As noted above, the small volume differences as the result of ortho vs. meta or para substitution have long been known. Furthermore, a number of studies (especially IR and Raman) of compounds with molecules in two conformational states have shown that pressure tends to enhance the populations of the more crowded conformers.¹⁵ The operation of a special steric factor on the volume parameter in chemical reactions has been known for a long time also,¹⁶ and the reasons for this (orbital interpenetration,¹⁷ Hammond postulate manifestation¹⁸) have been discussed. What had perhaps not been adequately realized is that major effects may be expected not only as a result of the steric confrontation of two very large groups, but also as a cumulative consequence of the interaction of many smaller ones. The aromatization of benzene valence isomers, with its enforcement of a state of close neighborliness of six groups, is a prime example.

Knowledge of the volume profile of chemical reactions, with its long and slow but accelerating history, is now reaching the stage

of application in the synthetic laboratory. For the most part the applications have been limited to reactions involving the multiple formation of bonds such as occurs in cycloaddition,¹⁹ but the present result suggests that the synthesis of crowded molecules may very well also become a major beneficiary of high-pressure application. While a tentative start with such applications has been made by Okamoto,²⁰ the present results make clear that they need not be limited to extremes involving *tert*-butyl substitution.

Experimental Section

Hexamethyl(Dewar benzene) was prepared by the aluminum chloride catalyzed trimerization²¹ of the 2-butyne obtained²² from 2,3-dibromobutane.²³ 1,2-Dihydrophthalic anhydride²⁴ was converted into Dewar benzene by the route developed by van Tamelen;²⁵ the product was purified by means of GLC (a Carbowax 20M column was used at 50–55 $^{\circ}\text{C}$). The isomerization of the former compound was studied in bromobenzene solution at $140 \pm 1 \text{ }^{\circ}\text{C}$, the latter in GLC-purified pyridine at $42.10 \pm 0.02 \text{ }^{\circ}\text{C}$. The conversion of **1a** was followed by means of NMR (Varian EM-360); anisole was used as an internal standard. The points were calculated on the basis of the assumption that the original concentration was the sum of those of **1a** and **2a**; in other words, the polymer formation was factored out. The side reaction was neither significantly increased nor depressed by the deliberate addition of milligram quantities of benzoyl peroxide or of pyridine. The aromatization of **1b** was studied by means of GLC; the data were corrected for the presence of unknown and stable material ($\sim 15\%$) which had the same retention time as **1a**.

The pressure equipment was described previously,²⁶ and the activation volumes were calculated in the usual way.² Partial molar volumes were determined with a pycnometer and technique previously described.²⁷ Both mesitylene and bromobenzene were used as solvents, and there was no significant variation of apparent molar volume with solvent or concentration. Samples of **1a** which had been completely converted were combined and evaporated to a small amount of residual liquid from which **2a** readily crystallized. Heating of the remaining tarry material to 250 $^{\circ}\text{C}$ for 4 h in an evacuated, sealed tube converted it into **2a** with a yield of about 50%.

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Registry No. **1a**, 7641-77-2; **1b**, 5649-95-6.

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