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Computational and Matrix Isolation Studies of Tetra-tert-butylethane

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Dedicated to Professor Dr. C. Rüchardt on the occasion of his 80th birthday

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Irradiation of cryogenic xenon matrices containing the sterically congested alkane tetra-*tert*-butylethane (1) with intense pulses from a KrF excimer laser ($\lambda_{exc} = 248$ nm) have resulted in the formation of methane and isobutene as the major products. Larger fragments derived from 1, such as 2,2-dimethylbutane (10), were also detected, whereas no evidence was obtained for the formation of the elusive tetra-*tert*-butylethylene (2). The results suggest that biphotonic irradiation of xenon matrices containing *tert*-butylated precursor molecules may generally result in the efficient formation of isobutene and smaller alkanes. An analysis of the decomposition

Introduction

Tetra-*tert*-butylethylene (2), one of the most sought-after molecules in organic chemistry, so far has remained resilient to all attempts at its synthesis.^[1] The naming of a book chapter on the synthesis of 2 as "... an exercise in preparative futility"^[2] may serve to illustrate the difficulties encountered in the synthesis of 2, which is otherwise predicted to be a reasonably stable molecule.^[3] Unsuccessful approaches to the preparation of 2 (Scheme 1) include the coupling of precursors containing a di-tert-butylmethyl moiety, such as di-tert-butyl selenoketone (3) and di-tert-butyldiazomethane (4),^[4a] the dimerization of matrix-isolated di-*tert*butylcarbene^[4b] or of radical ions of di-*tert*-butylcarbene^[4c] or the McMurry coupling of di-tert-butyl ketone (5).^[5] In other attempts, a "bent-back" approach was used.^[6] Tetrakis(1-methylcyclopropyl)ethene (6) can be synthesized, but the last step in the synthesis of 2, the hydrogenation of the cyclopropane rings, could not be achieved.^[1,2,7] An alternative, as yet untried approach is to take tetra-tert-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.200900378. reactions of **1** by various computational methods revealed that commonly used DFT methods, such as B3LYP or BLYP, and MP2 theory do not provide a good description of the energetics of the decay reactions of the sterically overloaded alkane **1**. The recently developed M05-2X method was the only method among those tested to yield an activation enthalpy for the cleavage of **1** in agreement with the experimental value.

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butylethane (1),^[8] a known molecule that already contains two adjacent di-*tert*-butylmethyl groups, and eliminate the two tertiary hydrogen atoms.



Scheme 1. Possible approaches to the synthesis of 2.

This contribution describes the attempts at the dehydrogenation of 1 by pyrolysis in cryogenic xenon matrices. The seminal work of Maier et al. showed that irradiation of bromine-doped Xe matrices with light from an Hg low-pressure lamp ($\lambda_{exc} = 254$ nm) results in the formation of XeBr exciplexes that are capable of transferring their excitation energy to a matrix-isolated guest molecule.^[9] The guest molecule thus may be locally heated at temperatures as low as 10 K, which results in a range of fragmentation reactions. A number of reactive intermediates, among them trimethylenemethane^[10] or the allyl radical,^[11] have been synthesized



this way. That the method can be used to dehydrogenate saturated species is evidenced by the fact that the Xe-matrix cryogenic pyrolysis of propane yields, among others, allene as a product.^[11] The use of bromine as a dopant can be avoided if high-energy pulses from a KrF excimer laser (λ_{exc} = 248 nm) are employed. Two-photon absorption of neat Xe results in the formation of Xe excimers, which release their energy to any matrix-isolated guest molecule in the form of thermal excitation.^[9] A necessary condition for this procedure is the absolute absence of any absorption of the matrix-isolated guest molecule at the excitation wavelength. This is fulfilled for **1**. For comparison, analogous irradiation experiments with **1** were also performed by using argon matrices.

Results

Matrix-Isolation Spectroscopy

Matrix isolation of 1 in Ar could be achieved at a sample temperature of 20 °C. The matrix containing 1 was subsequently irradiated by using both 248 nm irradiation from a KrF excimer laser and 193 nm irradiation from an ArF excimer laser. No photochemical conversion was observed: 1 proved to be absolutely photostable. If xenon was used as the matrix material, irradiation with high-energy pulses $(\lambda_{\text{exc}} = 248 \text{ nm}, \text{ ca. } 200 \text{ mJ/pulse})$ from a KrF excimer laser resulted in the slow disappearance of IR bands of 1 and the formation of a new infrared spectrum. It took a large number of laser pulses (65000) to achieve a nearly complete conversion of 1 into the new products.^[12] Figure S1 of the Supporting Information shows an infrared spectrum of 1 recorded in Xe, along with a calculated spectrum [B3LYP/ 6-31G(d)] for comparison. Figure S2 shows the infrared spectrum after the irradiation experiment.

Based on a comparison with literature data,^[13,14] a number of the newly formed IR bands can be assigned to methane ($\tilde{v} = 1300 \text{ cm}^{-1}$) and isobutene ($\tilde{v} = 1656, 1478, 891 \text{ cm}^{-1}$). A comparison of the experimental and calculated band integrals allows the ratio of methane/isobutene formed to be estimated as 1:3. As logical primary byproducts, tri-*tert*-butyl(isopropylidene)ethane **8** could be formed along with methane and tri-*tert*-butylethane **7** could be formed along with isobutene. The experimental spectrum in the range $\tilde{v} = 750-1500 \text{ cm}^{-1}$ is compared in Figure S3 with the calculated spectra of the possible products of demethylation and deisobutenylation.

Figure S3 indicates that an unambiguous assignment of product bands to individual product molecules is difficult. The low intensity of the product bands in the range $\tilde{v} = 1150-1250 \text{ cm}^{-1}$ shows that highly *tert*-butylated products such as 7, 8, 9 or 2 are not present in high concentrations as they are predicted to have prominent bands in this region. The agreement between the experimental product spectrum and the spectrum of 2,2-dimethylbutane (mono*tert*-butylethane; 10) appears to be the best. This is evidenced by the experimental band pattern (4:5:10 intensity ratio) between $\tilde{v} = 1410$ and 1360 cm^{-1} and the characteris-

tic weak double peak at $\tilde{v} = 990$ and 980 cm^{-1} , which only shows up in this form in the calculated spectrum of **10**. It is clear, however, that the product mixture also contains components other than methane, isobutene and **10**, as demonstrated, for example, by the broad and poorly resolved absorption at $\tilde{v} \approx 1450 \text{ cm}^{-1}$. The formation of some fragments can be ruled out conclusively. Ethane, as a possible final product of deisobutenylation, was not formed.^[15] No trace of the IR absorption attributable to tetra-*tert*-butylethylene (**2**) could be detected. According to the calculation, **2** should show one prominent IR band in a region (calcd. × 0.9614: $\tilde{v} = 1178 \text{ cm}^{-1}$) in which none of the other possible products should have a major IR band. The only candidate is a very weak IR band found at $\tilde{v} = 1179 \text{ cm}^{-1}$. This band, however, belongs to traces of unreacted precursor **1**.

Energy Calculations

Quantum mechanical calculations were performed to gain an insight into the thermodynamic feasibility of the fragmentation reactions that result from the thermal excitation of **1** and the subsequently formed products. The B3LYP hybrid functional^[16] usually yields useful geometries and infrared frequencies, whereas the energies obtained may be of questionable value, in particular if larger molecules are involved.^[17] For this reason, full geometry optimizations were also performed at the M05-2X/6-31G(d) and RIMP2/ cc-pVTZ levels of theory. No frequency calculations were attempted by using the RIMP2 method. Scheme 2 displays the results of the DFT and RIMP2 calculations.

As expected, the calculations indicate that the central C– C bond connecting the two di-*tert*-butylmethyl fragments should be the most prone to cleavage. Although this is consistent with the findings of Rüchardt and co-workers that heating of **1** in mesitylene at T = 141 °C leads to the formation of di-*tert*-butylmethane in good yield,^[8a] the bonddissociation enthalpies, as calculated by the three methods, are in such disagreement with each other that a thorough investigation into the choice of method seemed warranted.

To resolve the pronounced disagreement between the calculations, the homolytic cleavage of 1 into 2 equiv. of 14 was systematically investigated by using a variety of methods, including DFT methods, RIMP2 and Hartree–Fock theory with different basis sets. Table 1 shows the results.

According to Table 1, commonly used DFT methods such as B3LYP or BLYP vastly underestimate the activation enthalpy for the cleavage of 1 into 2 equiv. of 14. Increasing the size of the basis set is counterproductive with B3LYP or BLYP, as it results in a further decrease in the calculated BDE and activation enthalpy. The MP2 theory (both full MP2 and RIMP2), on the other hand, dramatically overestimates the stability of the central C–C bond in 1. Although no attempt was made to calculate the activation enthalpy for the cleavage of 1 by MP2 methods, the calculated bond dissociation enthalpies alone are significantly larger than the experimental value of ΔH^{\ddagger} . Again, no improvement was observed upon increasing the size of the basis set used. The



Scheme 2. Fragmentation pathways upon thermal excitation of 1 in Xe matrices. In italics: calculated enthalpies (RIMP2/cc-pVTZ, in kcalmol⁻¹) relative to 1 (0.0 kcalmol⁻¹). In parentheses: calculated entropies [B3LYP/6-31G(d), in calmol⁻¹ K⁻¹]. In ordinary font: calculated enthalpies [B3LYP/6-31G(d) + ZPE, in kcalmol⁻¹] relative to 1 (0.0 kcalmol⁻¹). Underlined: calcd. enthalpies [M05-2X/6-31G(d) + ZPE, in kcalmol⁻¹].

Table 1. Calculated activation enthalpies for the cleavage of 1 into 2 equiv. of 14, calculated BDEs of the central C–C bond in 1 and calculated bond lengths of the central C–C bond in 1.

Method	Basis set	BDE [kcalmol ⁻¹]	ΔH^{\ddagger} [kcal mol ⁻¹]	$R_{ m C-C}$ [Å]
HF + ZPE	6-31G(d)	25.2	n.c. ^[a]	1.632
	6-311++G(d,p)	26.5	n.c.	1.631
B3LYP + ZPE	6-31G(d)	11.4	27.6	1.636
	6-311++G(d,p)	8.3	26.9	1.632
BLYP + ZPE	6-31G(d)	10.2	22.4	1.654
	6-311++G(d,p)	5.8	21.4	1.650
M05-2X + ZPE	6-31G(d)	30.3	37.6	1.616
	6-311++G(d,p)	28.4	36.6	1.613
RIMP2	cc-pVDZ	48.8	n.c.	1.617
	aug-cc-pVDZ	61.9	n.c.	1.613
	cc-pVTZ	53.5	n.c.	1.606
MP2	cc-pVDZ	48.8	n.c.	1.616
Experiment ^[b]		n.k. ^[a]	36.4	n.k.

[a] n.c.: not calculated; n.k.: not known. [b] Ref.^[8a]

Hartree–Fock theory slightly underestimates the BDE, but yields better results than B3LYP, BLYP or MP2.

According to Table 1, the recently developed^[18] M05-2X method is the only method among those used in this study to correctly predict the activation enthalpy for the cleavage of 1. In combination with the 6-311++G(d,p) basis set, the calculated value of ΔH^{\ddagger} is 36.6 kcalmol⁻¹, which is in excellent agreement with the experimental value of $\Delta H^{\ddagger}_{exp}$ = 36.4 kcalmol⁻¹.^[8a] However, even by using the modest 6-31G(d) basis set, the result obtained with M05-2X is very good. The calculated value of ΔH^{\ddagger} = 36.6 kcalmol⁻¹ corresponds to a BDE of the central C–C bond in 1 of BDE = 28.4 kcalmol⁻¹ plus an activation enthalpy for the recombination of 2 equiv. of 14 of $\Delta H^{\ddagger}_{rec}$ = 8.2 kcalmol⁻¹. Note that this latter value is significantly below the lower limit

for the activation enthalpy ($\Delta H^{\ddagger}_{rec,exp} \ge 22.9 \text{ kcal mol}^{-1}$) reported by Ingold and co-workers.^[19]

The strain energy of 1 can be calculated by evaluating the isodesmic reaction given in Equation (1).

$$tBu_2CH-CHtBu_2 + 4 CH_3CH_3 \rightarrow Me_2CH-CHMe_2 + 4 C(CH_3)_4$$
 (1)

The strain energy obtained from Equation (1) [M05-2X/ 6-311++G(d,p)] is $H_s = 65.3 \text{ kcal mol}^{-1}$. This is in excellent agreement with the experimental value (obtained by measuring the heat of combustion of 1), which has been determined as $H_{s,exp} = 66.3 \text{ kcal mol}^{-1}$.^[8c] At the B3LYP/6-311++G(d,p) level of theory, the strain energy of 1 is calculated as $H_s = 76.3 \text{ kcal mol}^{-1}$, which is clearly too high. The fact that B3LYP and BLYP describe the energetics of **1** poorly suggests that these methods might also be unsuitable for calculating the strain energy of tetra-*tert*-butyl-ethene (**2**). The strain energy of **2** was therefore re-evaluated by calculating the isodesmic Equation $(2)^{[3]}$ at the M05-2X/ 6-311++G(d,p) level of theory.

$$tBu_2C=CtBu_2 + 4 CH_3CH_3 \rightarrow Me_2C=CMe_2 + 4 C(CH_3)_4$$
(2)

The strain energy of **2** thus calculated amounts to H_s = 81.2 kcalmol⁻¹ for the singlet-spin manifold and H_s = 35.3 kcalmol⁻¹ for the triplet-spin manifold, which is similar to the BLYP/Dzd values reported by Schleyer and Schaefer and co-workers.^[3] At the M05-2X/6-311++G(d,p) level of theory, the triplet enthalpy of **2** is obtained as ΔH_T = 11.7 kcalmol⁻¹, which is also in agreement with the value (12.6 kcalmol⁻¹) reported previously, and the C=C distance is 1.374 Å, which also fits well with the findings by Schleyer and Schaefer and co-workers.^[3]

Discussion

According to the results obtained by matrix isolation spectroscopy, the thermal decay of 1, matrix-isolated in Xe, takes place mostly by deisobutenylation and to a lesser degree by loss of methane. Literature evidence^[8a] as well as the calculations presented in this study suggest that the central C–C bond in 1 should be by far the most labile bond in 1. This reaction initially leads to a pair of di*-tert*-butylmethyl radicals 14. Unlike the radical pairs resulting from the fragmentation reactions around the periphery of 1, this radical pair cannot disproportionate into an alkane and an alkene. Subsequent reactions are therefore limited to recombination (I), the elimination of methyl radicals (II) or the disproportionation into di*-tert*-butylmethane and di*-tert*-butylcarbene (III), both of which may undergo further decomposition (Scheme 3).

Scheme 3 illustrates that the thermal cleavage of the central C–C bond in 1 might yield the same stable products (isobutene and methane) as the peripheral cleavage reac-

tions shown in Scheme 2. Note that the experimental data do not provide conclusive evidence for the formation of neopentane, which has a very simple IR spectrum (B3LYP/ $6-31G^*$: $\tilde{v}_{calcd.} = 1487, 1371, 1239 \text{ cm}^{-1}$).

The experimental data indicate that 2,2-dimethylbutane (10) is the most likely product formed upon complete decomposition of 1. This molecule is formed in a series of bond cleavage/radical-pair disproportionation reactions, resulting in a three-fold deisobutenylation of 1. The fact that ethane is not formed as a product is easily rationalized as its formation from 10 is predicted to be significantly endothermic (Scheme 2). Note, however, that the calculations predict 2,2,5,5-tetramethylhexane (9) to be the product formed, as deisobutenylation of 9 to yield 10 is also predicted to be endothermic. At present, this discrepancy between the computational and matrix isolation results cannot be resolved.

The M05-2X method gives excellent thermochemical data for 1, whereas other common DFT methods, such as B3LYP or BLYP, and MP2 theory do not. Table 1 shows that the stability of 1 and the length of its central C-C bond are related as a weak C-C bond corresponds to a long C-C bond. The length of this bond is a function of the interaction between the four tert-butyl groups placed around the two central carbon atoms. This interaction consists of both an attractive (dispersive interactions) and a repulsive component (strain). Commonly used DFT methods, such as BLYP or B3LYP, cannot describe dispersive interactions.^[20] They therefore underestimate the attractive component of the interaction and thus predict a C-C BDE and an activation enthalpy for cleavage of 1 that is too low. MP2 theory, on the other hand, in principle is capable of describing dispersive interactions, but overestimates their strength.^[21] It therefore overestimates the stability of **1**. Among the methods tested, only the M05-2X method appears to achieve the correct balance between attractive and repulsive intramolecular interactions in this molecule. Although the M05-2X results are in excellent agreement with the thermochemical data for 1 published by Rüchardt and co-workers,^[8] they are clearly inconsistent with the lower



Scheme 3. Possible decay channels upon initial thermal cleavage of the central C–C bond in 1. Δ refers to thermal excitation by interaction with an Xe exciplex.

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limit for the activation enthalpy for the dimerization of the di-*tert*-butylmethyl radical **14**, as measured by Ingold and co-workers employing ESR spectroscopy.^[19] At present, no explanation for this discrepancy can be offered.^[22]

Conclusions

Cryogenic pyrolysis of tetra-*tert*-butylethane (1), matrixisolated in xenon at T = 10 K, results in the multiple deisobutenylation of 1 with the likely formation of 2,2-dimethylbutane (10) in addition to isobutene and methane. Tetra*tert*-butylethene (2), however, is not formed. The data suggest that *tert*-butyl substituents may thus potentially be used as a protective group for matrix isolation spectroscopy, to be removed by thermal excitation in xenon matrices. Computational work performed on 1 indicates that the thermochemistry of this sterically highly overloaded alkane is poorly described by commonly used DFT, such as BLYP or B3LYP, and MP2 methods, whereas the recent M05-2X method yields energies in excellent agreement with published experimental data.

Experimental Section

Tetra-*tert***-butylethane (1):** This compound was synthesized by reductive coupling of 3-chloro-2,2,4,4-tetramethylpentane, as described by Rüchardt and co-workers.^[8a] In slight variation of the literature procedure, a commercial suspension of sodium metal in toluene was used as the sodium source. The yield thus achieved was higher than previously reported (up to 60%).

Matrix-Isolation Experiments: The matrix-isolation setup used has been described previously.^[23] Matrix-isolated samples of **1** in xenon or argon matrices were obtained by the slow-spray-on technique, with matrix temperatures $T_{depo} = 20$ (Xe) or 30 K (Ar) during deposition. Alkane **1** was kept at ambient temperature to allow for sufficient vapour pressure. The excitation of the matrices containing **1** was performed by using a Lambda-Physik Compex 100 excimer laser operated at 248 (KrF) or 193 nm (ArF). The pulse energy at $\lambda = 248$ nm (193 nm) was 200 mJ/pulse (100 mJ/pulse), with a repetition rate of 1 Hz.

Computational Methods: All DFT, MP2^[24] and Hartree–Fock calculations were performed by using the Gaussian03^[25] suite of programs. RIMP2^[26] optimizations with the cc-pVTZ, cc-pVDZ and aug-cc-pVDZ basis sets^[27] were performed by using the TUR-BOMOLE software.^[28] The DFT methods used include the BLYP functional,^[16] the B3LYP hybrid functional,^[16] and the M05-2X method,^[18] in combination with the 6-31G(d) and 6-311++G(d,p) basis sets.^[29] Transition-state structures for the dimerization of **14** were optimized by using the Gaussian keyword combination guess = (mix,always). The scaling factor (0.9614 for B3LYP) for the calculated infrared spectra was taken from the literature.^[30]

Supporting Information (see footnote on the first page of this article): Figures S1–S3, Cartesian coordinates and the energies of stationary points.

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