Photolysis of 2,2,3,3-Tetramethylbutane

S. K. Tokach and R. D. Koob*

Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105 (Received June 27, 1979)

The gas phase photolysis at 147 nm of 2,2,3,3-tetramethylbutane (hexamethylethane) gives the following primary products in decreasing order of importance: H, t-C₄H₉, i-C₄H₈, CH₃, i-C₄H₁₀, C₃H₆, CH₄, H₂. The final product distribution is readily interpreted by using known reactions of these primary fragments. Our interpretation indicates a considerably greater importance than found in an earlier examination by Gowenlock and Johnson for the role of *tert*-butyl radical. With the exception of isobutane, the molecular primary products parallel those found in earlier work by Rebbert, Lias, and Ausloos on neopentane.

Introduction

With the exception of neopentane^{1,2} the photochemical reaction of few highly branched alkanes have been extensively investigated. Among these, the photolysis of hexamethylethane has been reported.³ Quantum yields for products were not given, however, and only a qualitative interpretation of the photolysis mechanism was presented. In the absence of quantum yields, uncertainties may arise in separating intramolecular and free-radical reactions. Further, H₂S was used as a radical scavenger. Only a very small yield of $t-C_4H_9$ was intercepted, indicating that this intermediate played only a minor role in the reaction mechanism. Rebbert et al.² have found H_2S to be an inefficient scavenger for t-C₄H₉. Thus, it is likely that t-C₄H₉ is more important to the overall mechanism than indicated by Gowenlock and Johnson. Finally, we note the formation of several products depends on the percent conversion of parent to product. Previously reported results³ appear to represent a product distribution reflecting some internal scavenging of H atoms.

To extend the previous work, then, we have determined quantum yields for all observed products, used O_2 and HI as radical interceptors, and report yields at low enough conversion to assure secondary reactions with stable products are minor. Our evidence indicates that CH₃ and (CH₃)₃C play a considerably more important role in the reaction mechanism than suggested previously. Moreover, we are now able to give a quantitative reconciliation of postulated mechanistic yields.

Experimental Section

Hexamethylethane (Aldrich) was photolyzed at 147 nm by using a double-headed Xe resonance lamp, fitted with MgF₂ windows, as described in earlier work. A 2450-MHz Raytheon microwave generator was used to power the lamp. Quantum yields were determined by using ethylene actinometry. A $\Phi_{C_2H_2} = 0.90$ was assumed and the ratio of emission from each window was regularly measured. Standard vacuum techniques were used in sample preparation. Typical sample pressures of HME were 10 torr. Since a conversion dependence on some of the products was noted, irradiation times were varied from 120 s to 30 min.

Product analysis was done by FID gas chromatography. A 25-ft, 30% w/w squalane column separated all products containing C_1 – C_5 . Higher molecular weight products were not eluted. Retention times for each product were verified by authentic samples. Detector response was calibrated for all products.

For analysis of hydrogen, the sample reaction vessel, cooled to 77 K, was attached directly to a mass spectrom-

TABLE I: Φ Values for the Photolysis of HME

	Φ		
	neat	+ O ₂	+ HI
CH ₄	0.17 ± 0.03	0.09 ± 0.02	0.71 ± 0.08
C_2H_6 C_3H_6	0.18 ± 0.02 0.27 ± 0.03	0.26 ± 0.02	0.27 ± 0.03
C ₃ H	0.03 ± 0.01	0.06 - 0.09	1.04 + 0.10
$i \cdot C_4 H_{10}$ $i \cdot C_4 H_8$	0.42 ± 0.05 0.99 ± 0.11	0.26 ± 0.03 0.75 ± 0.07	0.76 ± 0.08
$neo-C_5H_{12}$	0.12 ± 0.02		

eter, Nuclide (3-60), inlet system. The noncondensable gases were then transferred to the inlet with a Toepler pump. Hydrogen was measured relative to CH_4 . As noted above CH_4 was also analyzed, in different samples, by gas chromatography.

All additives, including D_2S (Merck Sharpe and Dohme), HI (Linde), and O_2 (Linde), were used without further purification. In no case did additive concentrations of the sample mixture exceed 10%.

Results

The photolysis of 10 torr of pure HME yields the following seven products with the quantum yields indicated in parentheses: H₂ (~1.1), methane (0.17), ethane (0.18), propene (0.27), propane (0.03), isobutane (0.42), isobutene (0.99), and neopentane (0.12). The yields of all products, with the exception of propene, are decreased upon addition of O₂. Quantum yields in the presence of O₂ are as follows: hydrogen (~0.03), methane (0.09), propene (0.25), isobutane (0.26), isobutene (0.75). Ethane, propane, and neopentane production are completely suppressed by the O₂ addition. Yields reported are those corresponding to low conversions of HME to products.

Addition of small amounts (<10%) of HI results in reduction of the C_2H_6 , C_3H_8 , i- C_4H_8 , and neo- C_5H_{12} yields while the quantum yields of CH₄ and i- C_4H_{10} are increased to 0.71 and 1.04, respectively. The quantum yields of all products remain unchanged with addition of 450 torr of N₂ to the photolysis mixture. The quantum yield of carbon in observed products is

The quantum yield of carbon in observed products is 7.6. For unit quantum efficiency, a value of 8 would be expected. Since Gowenlock and Johnson report some heavier products, our failure to analyze for these products probably accounts for the shortfall. The quantum yield of observed hydrogen in products, less "abstracted" (secondary) hydrogen, is 7% higher than expected based on carbon. We have no obvious explanation for this excess, other than to note that our $\Phi(H_2)$ has larger than average uncertainty, that nonanalyzed heavier products are probably unsaturated, and that our average uncertainty in quantum yield measurements is about 16%.

Discussion

Stable Photoproducts. The quantum yields of products in oxygen scavenged experiments, Table I, are interpreted as arising from direct photodissociation of HME to stable molecules

HME
$$\xrightarrow{h\nu}$$
 H₂, CH₄, C₃H₆, *i*-C₄H₈, *i*-C₄H₁₀

or the dissociation of photofragments carrying excess energy. The absence of a pressure dependence in the range of 10-450 torr argues for the former interpretation. If secondary dissociation occurs, it is on a time scale faster than collision times in the higher pressure samples.

Specific assignment of fragments to their cofragments, i.e., identification of a given photoreaction, cannot be done without extensive labeling experiments. However, the high degree of symmetry of HME allows certain conclusions to be drawn concerning these intramolecular reactions. Compared to small alkanes, the molecular H₂ yield is very low, $\Phi = 0.03$. All H₂ must be produced from primary hydrogens in HME. CH_4 , $\Phi = 0.09$, can be produced only in a four- or five-member transition state and $i-C_4H_{10}$ can be produced only in a four-member transition state. This is noteworthy since three-center transition states predominate smaller acyclic alkane photolyses.⁴ Of all the products in Table I, only propene production is consistent with three-center fragmentation. Clearly, generalizations made from smaller acyclic alkanes cannot be extrapolated unmodified to larger highly branched molecules. On the other hand, there is a good deal of similarity between the photolyses of HME and neopentane.² Photodissociation at 147 nm of neopentane yields H_2 (0.02), CH_4 (0.22), C_3H_6 (0.15), and $i-C_4H_8$ (0.70). The only molecular product not found in neopentane that is important in HME is $i-C_4H_{10}$. To produce i-C₄H₁₀ from neopentane would require a CH₂ cofragment while i-C₄H₈ or other fragments are possible in HME. The large energy requirement to produce CH_2 effectively closes this reaction channel to neopentane.

The other notable difference between the results for neopentane and those reported here is the measurable pressure dependence of certain products in neopentane. A comparable pressure dependence was *not* found for HME. However, the experiments are not strictly comparable. Total pressure was varied, in the case of neopentane, by changing the sample pressure of neopentane. The same procedure was not possible with HME, a solid with 10 torr vapor pressure at room temperature. Thus, total pressure was varied for HME samples by adding nitrogen to the desired pressure. The efficiency of removal of energy by nitrogen may be enough less than that of neopentane that change in product quantum yields was insufficient to detect.

Radical Photoproducts. Both HI and O₂ are used here to intercept free radicals produced in HME photolysis with complementary results. Free radicals are expected to abstract a hydrogen from HI to form the analogous alkane. O₂ will form oxygenated products and these will not be detected by our analysis. The addition of HI enhances the yields of CH₄ to $\Phi_{CH_4} = 0.71$ and i-C₄H₁₀ to $\Phi_{i-C_4H_{10}} = 1.04$; the propene yield is left unchanged; the i-C₄H₈ yield is reduced to $\Phi_{i-C_4H_8} = 0.76$; and the yields of ethane, propane, and neopentane are reduced to zero. The addition of O₂ reduces all yields except propene. Hydrogen, methane, i-C₄H₁₀, and i-C₄H₈ yields are reduced to $\Phi_{H_2} = 0.03$, Φ_{CH_4} = 0.09, $\Phi_{i-C_4H_{10}} = 0.26$, and $\Phi_{i-C_4H_8} = 0.75$, respectively. Ethane, propene and neopentane yields are again reduced to zero. These observations are consistent with the direct photoproduction of H, CH₃, and t-C₄H₉. Total methyl radical yield, $\Phi_{CH_3} = 0.62$, is the difference between



Figure 1. The ratio of propene to isobutane as a function of conversion of parent to product.



Figure 2. The ratio of isobutene to isobutane as a function of conversion of parent to product.

methane quantum yields in the HI experiment and those in the oxygen experiment. Similarly, the total t-C₄H₉ yield, Φ_{t -C₄H₉ = 0.78, is the difference between the yield of isobutane in the presence of HI and isobutane in the presence of O₂. These total radical yields can be compared, for the sake of internal consistency, with the same yields predicted by the mechanisms for secondary radical reactions in the absence of additives as discussed in the following paragraphs.

Secondary Radical Reactions. If product concentrations are allowed to build by continued photolysis, the significant hydrogen atom yield begins to be internally scavenged by the unsaturated products. This is indicated by a significant conversion dependence of the propene/isobutane and isobutene/isobutane ratio in the neat system, Figures 1 and 2. Since $i-C_4H_8$ is the unsaturate produced in the highest yield, the effect on $i-C_4H_8$ and products having $t-C_4H_9$ radical precursors is most marked. At very low conversion, hydrogen atoms are assumed to react by abstracting a hydrogen from HME to form H₂. Thus the scavengeable quantum yield of H₂ at low conversion is equated to primary hydrogen atom production. Hydrogen atom production is large compared to molecular hydrogen yield. This parallels findings in neopentane.

Methyl radicals, on the other hand, appear to undergo radical-radical reactions with other methyl or *tert*-butyl radicals and do not appear to abstract hydrogen from HME. Further comment on this will be made below.

Methyl radicals contribute to three products, CH_4 , C_2H_6 , and neo- C_5H_{12} , by disproportionation and combination reactions.

8 The Journal of Physical Chemistry, Vol. 84, No. 1, 1980

$$CH_3 + t - C_4 H_9 \rightarrow CH_4 + i - C_4 H_8 \tag{1}$$

$$CH_3 + t - C_4 H_9 \rightarrow neo - C_5 H_{10} \tag{2}$$

$$2CH_3 \rightarrow C_2 H_6 \tag{3}$$

The quantum yield for each reaction is obtained by taking the difference between the yield of the italicized product in the neat and O₂ trapped photolyses. Thus, the mechanism predicts the following quantum yields for methyl: $\Phi_{\rm CH_3}^{(1)} = 0.08, \Phi_{\rm CH_3}^{(2)} = 0.12, \text{ and } \Phi_{\rm CH_3}^{(3)} = 2 \times 0.18.$ The superscript on each Φ indicates the appropriate postulated reaction. The sum of these reactions, plus a small CH_3 contribution obtained from C_3H_8 (all removed by O_2) of 0.03, is 0.59 \pm 0.06, in acceptable agreement with measured methyl yield, $\Phi_{CH_3}^{meas} = 0.62 \pm 0.08$, noted in the previous sections. Further, the ratio of quantum yields of methane to neopentane should provide a measure of the disproportionation/combination (D/C) ratio for methyl and *tert*-butyl. That is D/C = 0.67. This value, while close to the range of published values,⁵ is low if anything. This substantiates to some degree the assumption that CH₃ does not abstract hydrogen from HME to any appreciable degree, as an additional free radical source of methane would give an apparently high value for D/C.

In addition to the disproportionation and combination reactions with methyl, reactions 1 and 2, *tert*-butyl can undergo self-disproportionation and combination, reactions 4 and 5. The quantum yield assigned to reaction 4 is the

$$2t \cdot C_4 H_9 \rightarrow i \cdot C_4 H_{10} + i \cdot C_4 H_8 \tag{4}$$

$$2t - C_4 H_9 \rightarrow HME$$
 (5)

difference in isobutane yield in the presence and absence of O_2 , $\Phi_{i\cdot C_4H_{10}}$ radical = 0.16. The sum of yields assigned to reactions 1 and 4, $\Phi^{(1)} + \Phi^{(4)} = 0.24$, should account for all radical-derived isobutene. The isobutene coming from radical reactions is measured by the difference between isobutene yields in the presence and absence of O_2 at low conversions. Referring to columns 1 and 2 of Table I, we note that this difference is 0.24 in excellent agreement with our expectation.

Further support for our assignment is obtained by summing all *tert*-butyl from the mechanistic steps (1), (2), and (4), obtaining the quantum yield for reaction 5 by difference between that sum and the total measured *tert*-butyl from the HI addition experiments. The ratio of quantum yields for reactions 4 and 5 is a measure of D/C for *tert*-butyl. These operations give $\Phi_{\rm HME}^{(5)} = 0.13$ and D/C = 1.2. A very wide range of D/C for *tert*-butyl is reported, all greater than unity, so a comparison is difficult.⁵ However, our D/C value is again somewhat lower than the average reported values.

Overall, the analysis reproduces known values sufficiently well that we assign the following yields to the primary photoproducts for HME in order of their importance:

$$\begin{array}{cccc} \text{HME} & \stackrel{h\nu}{\longrightarrow} \text{H} & & \sim 1.0 \\ & t\text{-}\text{C}_4\text{H}_9 & & 0.78 \pm 0.10 \\ & i\text{-}\text{C}_4\text{H}_8 & & 0.75 \pm 0.07 \\ & \text{CH}_3 & & 0.62 \pm 0.08 \\ & i\text{-}\text{C}_4\text{H}_{10} & & 0.26 \pm 0.03 \\ & & \text{C}_3\text{H}_6 & & 0.26 \pm 0.02 \\ & & \text{CH}_4 & & 0.09 \pm 0.02 \\ & & \text{H}_2 & & \sim 0.03 \end{array}$$

 Φ

Scheme I: Summary of Products Involving Methyl Radicals



Scheme II: Summary of Products Involving tert-Butyl Radicals



Schemes I and II illustrate and summarize, in a graphical fashion, the discussion leading to the primary photoproduct yield assignments.

To a high level of correspondence this examination of the photochemistry of hexamethylethane confirms the conclusions, drawn from a study of neopentane, of Rebbert, Lias, and Ausloos contrasting photoreactions of normal and highly branched alkanes. Moreover, good internal consistency is obtained between titrated free-radical yields and yields of the same species predicted from known reactions of thermal free radicals.

Two aspects of our evaluation perhaps are cause for concern and further work.

Although the total quantum yield for the loss of HME based on summing over products observed in the neat photolysis is less than one, our mechanistic interpretation requires a quantum yield for loss of HME somewhat greater than unity. Uncertainties in measurements are large enough to account for this variation; nonetheless, one would be more comfortable with a somewhat lower total.

While we pointed out at the beginning that our data were inadequate to the task of assigning specific primary photoreactions to this system, attempts to do so point out an immediate difficulty, the high yield of methyl radical is difficult to reconcile with the yield and nature of the other fragments observed. This observation, coupled with the hydrogen-rich mass balance, caused us to carefully examine our experimental procedure for systematic error with respect to CH₃. Nothing was found to suggest that the relative yields were unreliable. Absolute quantum

yields are based on published actinometers and we cannot directly attest to their accuracy.

References and Notes

- Lias, S. G.; Ausloos, P. J. Chem. Phys. 1966, 43, 2748.
 Rebbert, R. E.; Lias, S. G.; Ausloos, P. J. Photochem. 1975, 4, 121. Gowenlock, B. G. Johnson, C. A. F. J. Chem. Soc., Perkin Trans. 2 1972, 2, 1150. ÌΞ)
- Ausloos, P.; Lias, S. G. "Chemical Spectroscopy and Photochemistry in the Vacuum-Ultraviolet"; Sandorfy; Ausloos, Robin; Ed.; Reidi (4)Publishing Co.: Boston, Mass., 1974; p 465. Trotmen-Dickenson, A. F.; Milne, G. S. *Nat. Bur. Stand.*, (U.S.) 1967.

Gas-Phase Pyrolysis Kinetics of 2-Substituted-2-Propyl Acetates. Effect of Substituents on the α -Carbon of Tertiary Acetates

Ignacio Martín, Gabriel Chuchani,* Irama Avila, Alexandra Rotinov, and Rolando Olmos

Centro de Química, Instituto Venezolano de Investigaciones Científicas, Apartado 1827, Caracas, Venezuela (Received March 20, 1979; Revised Manuscript Received August 7, 1979)

Publication costs assisted by the Instituto Venezolano de Investigaciones Científicas, Caracas, Venezuela

Three 2-substituted-2-propyl acetates undergo a homogeneous, first-order, unimolecular elimination in the gas phase at temperatures from 230 to 340 °C and pressures from 56 to 210 mmHg. The rate constants are expressible by the Arrhenius equation: for 2,3,3-trimethyl-2-butyl acetate, $\log k$ (s⁻¹) = (14.40 ± 0.49) - (171.5 ± 4.6) kJ mol^{-1} (2.303*RT*)⁻¹; for α -acetoxyisobutyronitrile, log k (s⁻¹) = (14.45 ± 0.82) - (198.7 ± 8.8) kJ mol⁻¹ (2.303*RT*)⁻¹; for methyl α -acetoxyisobutyrate, log $k(s^{-1}) = (12.53 \pm 0.32) - (176.1 \pm 3.6)$ kJ mol⁻¹ $(2.303RT)^{-1}$. The Taft correlation for the pyrolyses of tertiary esters with substituents on the α -carbon is projected and discussed. Many of these substituents enhance the elimination by steric acceleration.

Introduction

Structure-reactivity relationships have successfully been used in studies of unimolecular gas-phase pyrolyses of esters.¹⁻⁷ Various linear correlations for 1 with substituents



on the benzene ring remote to the reaction center have provided an adequate picture of the very discrete polarity of the transition state during the process of molecular elimination of these compounds. Very few aliphatic systems have been linearly correlated. The log of $k_{\rm rel}$ for the pyrolysis of β -substituted ethyl acetates against \vec{E}_s values gave an approximate straight line (r = 0.913), indicating that steric acceleration is important in determining the rate.8

Although several works have described the effect of substituents at the α position on the alcoholic part of aliphatic esters, it seemed worthwhile to gather and add, to a certain extent, more data to see whether any possible linear free energy relationship is consistent and conclusive with the nature of the transition state for these reactions. Therefore, the present work describes the study of the effect of substituents Z in the 2-position of aliphatic 2substituted-2-propyl acetates (2), especially with some electron-withdrawing groups, and how they affect these elimination reactions. The compounds of study are

2,3,3-trimethyl-2-butyl acetate, α -acetoxyisobutyronitrile, and methyl α -acetoxyisobutyrate.

Experimental Section

The alcohols 2,3,3-trimethyl-2-butanol, acetone cyanohydrin, and methyl α -hydroxyisobutyrate were treated with ketene gas to yield the corresponding acetates. The ketene gas was generated "in situ" as described.⁹ The esters obtained were 2,3,3-trimethyl-2-butyl acetate (bp 70 °C (30 mmHg); lit.¹⁰ 139–140 °C), α -acetoxyisobutyronitrile (bp 86 °C (23 mmHg)¹¹); and methyl α -acetoxyisobutyrate (bp 169-171 °C (630 mmHg); lit.¹¹ 76-77 °C (18 mmHg)). These acetates were redistilled several times and the fraction of at least 98.7% purity (gas-liquid chromatography) was used (7% FFAP-Chromosorb W AW DMCS, 80-100 mesh). The commercially acquired olefins 2,3,3-trimethyl-1-butene (Aldrich Chemicals), methacrylonitrile (Merck Schuchardt), and methyl methacrylate (Merck Schuchardt) were over 99.0% and were used as standard reference materials. The same FFAP column was used for the pyrolysis products analyses. The acetic acid product was titrated with 0.05 N sodium hydroxide solution. The purity and identity of these compounds were checked with a mass spectrometer and by infrared and nuclear magnetic resonance spectroscopy. The least-squares calculations were done with a Digital PDP 1145 computer.

Kinetic measurements were carried out in a static system and the reactions were followed manometrically. Vessels seasoned by the products of decomposition of allyl bromide^{12,13} were employed in this work.