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PARTIAL DEGRADATION OF 1,3,5-CYCLOHEPTATRIENE-14C OBTAINED FROM HOT-ATOM.,
PHOTOLYTIC, AND "THERMAL" REACTIONS

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PARTIAL DEGRADATION OF 1,3,5-CYCLOHEPTATRIENE-¹⁴C OBTAINED FROM
HOT-ATOM, PHOTOLYTIC, AND "THERMAL" REACTIONS

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1,3,5-Cycloheptatriene-¹⁴C (CHT), one of the prominent products of fast ¹⁴C atoms in benzene, was produced with ¹⁴C⁺-ions (kinetic energies of 5, 31, and 100 eV) and was partially degraded. In the 5-100 eV energy range, over which the yield varies by a factor of about 6 to 8, the distribution of ¹⁴C-activity in the CHT product seems constant, i.e. 31% in carbons 2-5. This value is compared with 45% obtained from 5000 eV ¹⁴C⁺-ions, indicating secondary isomerization of CHT-¹⁴C, at the higher energy, after its formation. In contrast, these same four carbons contain only 3.5% of the activity in CHT prepared by the photolysis of ¹⁴CH₂N₂ in benzene, and only 2.5% of the activity when the CHT is prepared by the catalytic decomposition of ¹⁴CH₂N₂ in benzene. It is concluded that (1) over the energy range from 5 to 100 eV only one mechanism is operative, (2) the last step, presumably the insertion reaction of CH₂ into benzene, does not proceed at energies above 5 eV, and (3) the effective energy available to the photochemically produced CH₂ must be well below 5 eV.

Introduction

(1,2) A fast carbon ion entering a solid benzene target is neutralized and, when its energy is less than 100 eV, it begins to pick-up hydrogen atoms from benzene molecules, forming CH_n radicals, of which CH_2 has been assumed to be the precursor to cycloheptatriene (CHT).^{1,2} In the preceding paper we have indicated that hydrogen pick-up may occur over a wide energy range, extending possibly up to 100 eV.³ This was concluded from the rapid decrease of the yield of CHT when the irradiating $^{14}\text{C}^+$ -ion's energy was decreased from 100 to 5 eV. However, our data is not extensive enough to rule out participation of other radicals, such as CH and CH_3 .

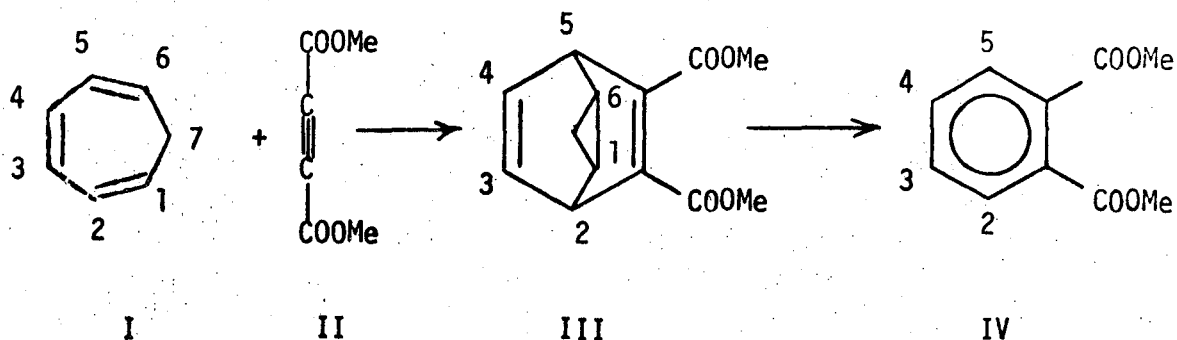
(3) CHT has been shown to be extensively isomerized if formed from $^{14}\text{C}^+$ -ions of 5000 eV energy.² In the preceding paper,³ it was also concluded that insertion reactions, such as that of CH_2 leading to CHT, have to occur below 5 eV. In other words, the range from 5 eV to 100 eV concerns only the formation of precursors. However, if there were more than one precursor involved (for example, a CH radical) in the formation of CHT, the relative abundances of these precursors would be expected to change and, very likely also, the degree of isomerization of CHT. We have, therefore, carried out the partial degradations of CHT obtained with $^{14}\text{C}^+$ -ions between 5 and 100 eV. For comparison, ^{14}C -CHT products from benzene and $^{14}\text{CH}_2$ via two different methods^{4,5} ("thermal" and "photolytic") were also partially degraded.

Experimental Details and Results

(4,5) The procedures for the irradiations and for the isolation of CHT- ^{14}C have been described previously.² (For technical details concerning the

ion accelerator see Refs. 6 and 7.)

The degradation procedure involves:



For experimental details see Refs. 2 and 6. The ratio of specific activities of IV to III (or I) represents the relative abundance of labeling in positions 2, 3, 4, and 5 together. This ratio, in %, is denoted by α .

Catalytic Decomposition of $^{14}\text{C}_2\text{N}_2$. See Ref. 2.

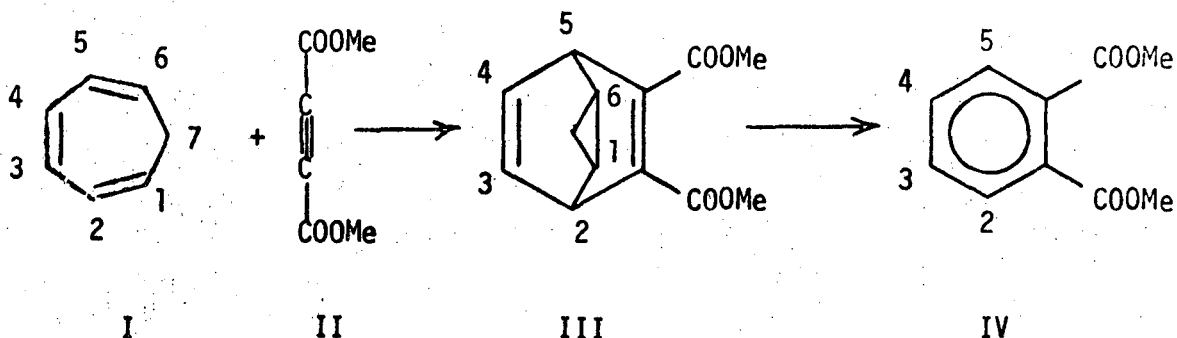
Photolytic Preparation of ^{14}C -CHT. Nitroso-methyl- ^{14}C -urea (20 g, sp. act. 10.8×10^5 dpm/mmole) was added slowly to 400 ml of benzene above a solution of 60 g KOH in 60 ml H_2O at ca. 6° . At the completion of the hydrolysis the yellow CH_2N_2 solution was decanted and irradiated at 6° for 4 hrs. with an unfiltered G.E. DXB "Photospot" lamp at about 20 cm distance. The isolation of ^{14}C -CHT was performed, as in Ref. 2, via preparative glpc; this is sample A.

Half of the above photolysis reaction mixture was irradiated under the same conditions for another 4 hrs. in order to check on possible isomerization of $\text{CHT-}^{14}\text{C}$ after formation; this is sample B.

The values for α given in Table I, together with that reported earlier for a 5000 eV irradiation,² are plotted in Figure 1.

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Photolytic Preparation of ^{14}C -CHT. Nitroso-methyl- ^{14}C -urea (20 g, sp. act. 10.8×10^5 dpm/mole) was added slowly to 400 ml of benzene above a solution of 60 g KOH in 60 ml H_2O at ca. 6° . At the completion of the hydrolysis the yellow CH_2N_2 solution was decanted and irradiated at 6° for 4 hrs. with an unfiltered G.E. DXB "Photospot" lamp at about 20 cm distance. The isolation of ^{14}C -CHT was performed, as in Ref. 2, via preparative glpc; this is sample A.

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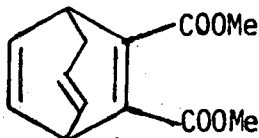
The values for α given in Table I, together with that reported earlier for a 5000 eV irradiation,² are plotted in Figure 1.

Table I: Degradation of the Cycloheptatriene from Accelerated $^{14}\text{C}^+$ and Photolyzed $^{14}\text{CH}_2\text{N}_2$.

Sample designation (and source)	Compound	Weight (mg)	Spec. Act. dpm/mole	Average α (%)
A (photolytic prep.)	I	0.339	11.1×10^8	4.06%**
	III _a *	3.806	11.7×10^8	
		5.915	11.7×10^8	
	IV	3.787	4.92×10^7	
		2.497	4.59×10^7	
B (photolytic prep.)	IV	2.841	4.13×10^7	3.52%
		0.547	4.15×10^7	
(100 eV $^{14}\text{C}^+$ -ions)	III	3.497	5.87×10^7	31.3%
	III _a *	3.686	5.94×10^7	
		3.244	5.97×10^7	
		4.156	5.93×10^7	
	IV	1.821	1.87×10^7	
		3.450	1.86×10^7	
2.94		1.88×10^7		
(31 eV $^{14}\text{C}^+$ -ions)	III _a *	4.161	9.15×10^7	30.0%
		4.090	9.00×10^7	
		4.428	9.23×10^7	
	IV	3.676	2.73×10^7	
		3.443	2.70×10^7	
		4.188	2.79×10^7	
(5 eV $^{14}\text{C}^+$ -ions)	III _a *	5.196	4.8×10^7	33.6%
		1.161	5.22×10^7	
	IV	3.236	1.695×10^7	
		3.172	1.71×10^7	
		2.860	1.68×10^7	

Footnotes to Table I:

- *) IIIa is an isomer of III which does not decompose to IV (see Refs. 2 and 6). Its structure is most likely:



- ***) The somewhat higher degree of isomerization in sample A is probably due to an accidental heating of the "buffer" of the Prepmaster, which was avoided in the isolation of sample B. Therefore, we have taken 3.5% as the upper limit for both A and B.

Discussion

If there is a real increase in α for energies higher than 100 eV (as is indicated by Figure 1), this increase may be due to increased "radiation damage" at the higher energies where the terminal "hot spot" will be larger. That is, there may be available, from diffusional processes at the end of the accelerated carbon's track, additional fragments, such as hydrogen atoms, whose availability may increase the yield of CHT.

Our interpretation of the yield drop from 2.5% at 100 eV to 0.3% at 5 eV is that in this range precursors, presumably CH_2 , are formed which produce CHT by insertion into the benzene ring.³ Fewer of these precursors would be formed at the lower energies, where, for example, a bare carbon might interact with benzene before it could become CH_2 . If this is correct and if α is a measure of the degree of isomerization (via hydrogen shifts) of CHT during or following the insertion reaction,² the constancy

of α between 5 and 100 eV implies that the energy at which a CHT precursor (CH_2) reacts with benzene does not reflect the energy at which the precursor was formed. Therefore, the upper energy limit for insertion with appreciable success has to be below 5 eV. This constancy also implies that a possible "low energy mechanism" for CHT, such as insertion of C or CH into benzene--followed by hydrogen pick-up,² cannot contribute appreciably to the formation of CHT/because its relative contribution should have increased considerably at 5 eV. Since the CHT yield has decreased by a factor of 8 compared to what it is at 100 eV, the value of α should have changed unless both mechanisms produce separately exactly the same α . This is very unlikely.

(8) The comparison of the "hot-atom" α with that of photolytically and catalytically produced CHT (3.5 and 2.5%, respectively)² suggests that either we are dealing with a different mechanism in the "hot-atom" case (which may be a difference in the electronic states of CH_2) or that the energy distribution of photolytically produced CH_2 is confined to a much lower energy range than that of hot-atom chemically produced CH_2 . These are estimates for photolytic CH_2 energies between 0.5 and 1.7 eV.⁸ Since this energy does not seem sufficient to cause appreciable isomerization of CHT, nor of CHT to toluene,⁹ the CHT obtained in the hot-atom chemical system must have been produced by CH_2 with energies well above 1.7 eV but below ca. 5 eV. Doering and Gaspar¹⁰ found a certain amount of deuterium, in carbons 1-6 of CHT prepared photolytically from CD_2N_2 ; however, they seem to attribute it mainly to photoisomerization of CHT after its formation.

The most reasonable interpretation of our results is that only one mechanism is operable for the CHT production, and that CH_2 radicals with energies between about 0.5 and 4 eV are the precursors. Some of these precursors with energies >1.7 eV cause considerable isomerization in the CHT product.

Acknowledgements

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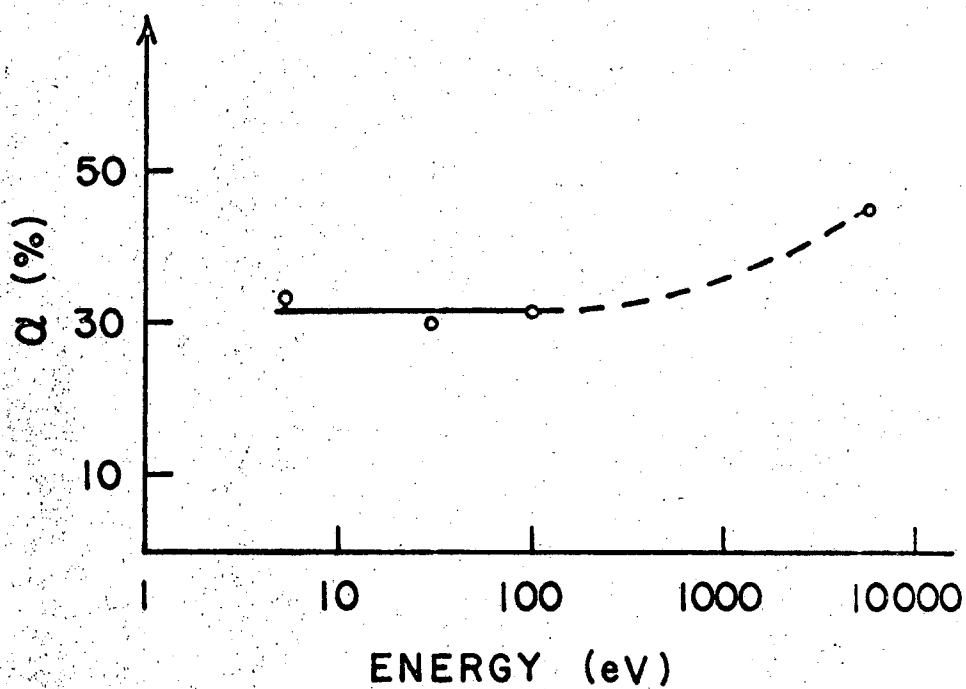


Figure 1. ^{14}C -labeling in positions 2, 3, 4 and 5 of ^{14}C -cycloheptatriene versus $^{14}\text{C}^+$ -ion energy.

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