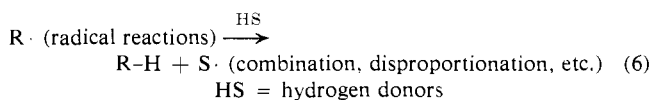
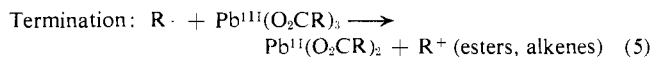
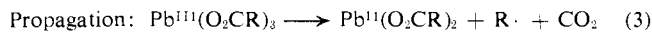
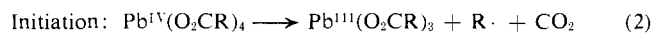
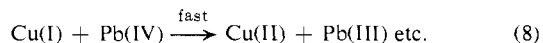
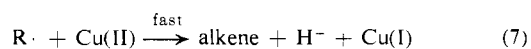


secondary acid, after inhibition by oxygen, will reinitiate itself after several hours.

The marked and reversible inhibition by oxygen, the catalysis by copper salts and valeryl peroxide, and the nature of the products of decomposition are strong support for a mechanism which involves a free radical chain process, and *lead(III) is implicated as an intermediate*.⁶ The following sequence is proposed



Such a mechanism can readily account for the catalysis by copper salts. Alkyl radicals are known to be scavenged effectively by Cu(II) to form alkenes (eq. 7).⁸ Cu(I) is subsequently reoxidized (eq. 8) by Pb(IV)



to regenerate Cu(II) and the metastable Pb(III) intermediate. The latter reaction is also rapid since lead(IV) carboxylates are instantaneously reduced by Cu(I) at room temperature. In this manner the slower oxidation of alkyl radicals by Pb(IV) in the propagation step (4) is circumvented and alkenes characteristic of Cu(II) oxidations⁵ are major products. The butyl radical from valeric acid also can be trapped⁹ with butadiene to yield a mixture of 1-acetoxyoctene-2 and 3-acetoxyoctene-1, and *sec*-butyl radical from 2-methylbutyric acid can also be diverted with oxygen to afford a mixture of methyl ethyl ketone and *sec*-butyl alcohol.

The key reactions in the proposed chain process are the propagation steps (3) and (4). The spontaneous dissociation (3) of the metastable Pb(III) intermediate is similar to that postulated for the fragmentation of triethyllead(III) during reduction of triethyllead(IV).¹⁰ The rates of oxidation (4) of alkyl radicals by Pb(IV) are dependent on the structure of R in accord with their ionization potentials.¹¹ Thus, secondary and tertiary radicals are largely oxidized to esters, alkenes, and products derived from carbonium ion intermediates. 2-Methylbutyric acid forms *sec*-butyl acetate (25%) and 2-methylbutyrate (35%) in good yield, together with a mixture of butene-1 (7%), *cis*- (4%) and *trans*- (8%) butene-2, *n*-butane (9%), and *sec*-butylbenzene (10%). In contrast, the primary isovaleric and valeric acids give mainly products such

(6) Studies to identify Pb(III) intermediates are in progress. Other mechanisms without Pb(III) can be considered at the sacrifice of simplicity.

(7) R⁺ denotes formal oxidation state only. Equations balanced as esters (R' O₂CR) or alkenes (C₂H₄ + HO₂CR), etc.

(8) J. K. Kochi, *J. Am. Chem. Soc.*, **85**, 1958 (1963); H. E. DeLamare, J. K. Kochi, and F. F. Rust, *ibid.*, **85**, 1437 (1963).

(9) J. K. Kochi and H. E. Mains, *J. Org. Chem.*, **30**, in press.

(10) C.-H. Wang, P. L. Levins, and H. G. Parrs, *Tetrahedron Letters*, 687 (1964).

(11) From the gas phase, R. Taubert and F. P. Lossing, *J. Am. Chem. Soc.*, **84**, 1525 (1962).

as isobutane (30–40%) and *n*-butane (10–20%), and minor amounts of butenes, together with isobutylbenzene (10%) and *n*-butylbenzene (20%), respectively, due to the slower oxidation (eq. 4) of primary radicals and competition from other facile radical reactions (eq. 6). Esters are significant but minor products (1–10%).

We postulate that there is a unity of mechanism which pertains to decarboxylation of carboxylic acids generally.^{1–4,12} The spectrum of products obtainable with diverse acids is attributable to varying efficiencies of the initiation and particularly the propagation steps with the structure of the acid. The roles of ligand transfer and electron transfer in the oxidation steps (4 and 5), and the preparative value of Pb(IV) decarboxylations in the presence of Cu salts, will be presented later.

Acknowledgment. The author wishes to thank the National Science Foundation for generous financial assistance of this work.

(12) In following studies we hope to demonstrate the general applicability of mechanism 2–6 to decarboxylations of other acids (with the possible exception of formic acid) and a related mechanism to other substrates.

Jay K. Kochi

Department of Chemistry, Case Institute of Technology
Cleveland, Ohio 44106

Received January 15, 1965

Reactions of Thermal Carbon Atoms¹

Sir:

We have bombarded 99.999% zone-refined benzene frozen on a liquid nitrogen cooled surface with carbon fragments from carbon vapor.² Gas chromatographic analysis of the irradiated benzene shows toluene and cycloheptatriene to be among the reaction products. It seems most probable that these products result from the reaction of benzene with thermal carbon atoms.

The carbon vapor was obtained by electrically heating a spectrographic quality carbon rod mounted centrally in the 500-ml. bombardment flask, which was evacuated to a pressure of 0.1 to 1.0 μ during all bombardments. Benzene (*ca.* 0.003 ml.) was introduced into the flask as vapor mixed with He so as to be diffusion blocked. After a 1-min. period for condensation of benzene on the liquid nitrogen cooled walls, any uncondensed benzene and the He were pumped off. The rod was then turned on and the benzene bombarded with carbon vapor for 180 sec. All experiments consisted of 20 such successive bombardments. In some experiments the benzene was vaporized and collected in a cold finger between each bombardment. In others it was not vaporized until all 20 bombardments had been run. After completion of the 20 bombardments, the 0.06 ml.

(1) (a) This research was supported by the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research, Grant No. AF-AFOSR-245-65; (b) research sponsored by U. S. Army Research Office (Durham) Grant No. DA-ARO(D)-31-124-G-271.

(2) The composition of carbon vapor under equilibrium and non-equilibrium conditions has been extensively investigated.³ Under non-equilibrium conditions the relative surface evaporation rates of the three most abundant constituents of carbon vapor, C₁, C₂, and C₃, are 1.0, 1.0, and 1.6³⁰ at 2500°K.

(3) (a) R. J. Thorn and G. H. Winslow, *J. Chem. Phys.*, **26**, 186 (1957); (b) J. Drowart, R. P. Burns, G. DeMaria, and M. G. Inghram, *ibid.*, **31**, 1131 (1959); (c) R. P. Burns, A. J. Jason, and M. G. Inghram, *ibid.*, **40**, 1161 (1964).

Table I. Summary of Results

	1	2	3	4	5	6	7
Rod temp., °K. ^a	1893	2122	2225	2253	2320	2353	2390
Rod surface area, cm. ²	7.5	6.6	6.6	7.5	6.6	7.5	6.9
Carbon evap. rate, g./cm. ² sec. ^b	3.3×10^{-13}	8.4×10^{-11}	2.3×10^{-10}	2.3×10^{-9}	8.8×10^{-9}	1.6×10^{-8}	3.5×10^{-8}
Total carbon evaporated, g.	8.9×10^{-9}	2.0×10^{-8}	1.8×10^{-8}	6.2×10^{-8}	2.1×10^{-7}	4.3×10^{-7}	8.7×10^{-7}
Concn. identified products, M ^c	<i>d</i>	<i>d</i>	2.1×10^{-5}	4.9×10^{-5}	1.1×10^{-4}	<i>d</i>	<i>d</i>
Concn. toluene	<i>d</i>	<i>d</i>	$\sim 2 \times 10^{-5}$ ^e	8.6×10^{-4}	4.2×10^{-5}	<i>d</i>	<i>d</i>
Concn. cycloheptatriene	<i>d</i>	<i>d</i>	$\sim 2 \times 10^{-5}$ ^e	8.6×10^{-4}	4.2×10^{-5}	<i>d</i>	<i>d</i>

^a Measured by optical pyrometry. ^b The carbon evaporation rate data used were from the work of M. Hock, P. Blackburn, D. Dingley, and H. Johnston, *J. Phys. Chem.*, **59**, 97 (1955). ^c Product yields were determined by comparison of peak heights from standards; peak heights for toluene and cycloheptatriene are linear in concentration over the concentration range 3×10^{-1} to 3×10^{-5} M. ^d Product yield was less than the limits of detection, which are 8.8×10^{-6} M for toluene and 1.8×10^{-5} M for cycloheptatriene for 2- μ l. injections. ^e This yield was just barely above the limit of detection.

of bombarded benzene was collected by vaporization and condensation in a liquid nitrogen cooled cold finger, which was sealed under vacuum. Chromatographic product analyses were performed using silicone oil columns and flame ionization detection. Products were identified by comparison of their relative retention times (relative to the solvent benzene peak) with those of knowns in benzene solution. The experimental results are summarized in Table I.

As is shown in the table, despite a constantly increasing rate of carbon deposition the yields of toluene and cycloheptatriene increased for only the first four runs before falling below their detection limits during the next three runs. Further, whenever the total carbon deposited per irradiation was greater than 3×10^{-6} g.⁴ (*i.e.*, runs 4 thru 7), a dark brown material was observed to form on the walls of the bombardment flask during the course of the experiment. Qualitatively, the yield of this material, which was nonvolatile at 1 μ even when heated to *ca.* 50°, increased rapidly with increasing carbon deposition per irradiation. Thus, as the yield of this material increased, the yields of toluene and cycloheptatriene fell below their limits of detection.

That the toluene and cycloheptatriene were not produced by photolysis or pyrolysis of the benzene under the conditions of our experiments is demonstrated by runs 1 and 2 at 1893°K. and 2122°K. In these runs carbon evaporation rates were too low to lead to detectable product levels. However, the operating temperatures of run 1 and particularly of run 2 were not sufficiently different from our normal operating temperatures to effect significantly the yields of products formed by photolysis or pyrolysis. Thus, the failure to detect toluene or cycloheptatriene in either run eliminates the possibility that they were formed by photolysis or pyrolysis.

Skell has reported previously that C₃ from carbon vapor reacts with isobutylene to form 1,1,1',1'-tetramethylbisethanoallene.⁵ The present work provides the first example of reaction of C₁ from carbon vapor with an organic substrate.^{5a}

Nuclear transformations have been used extensively

(4) It is interesting to note that this amount of carbon contains approximately the same number of carbon fragments as there are surface benzene molecules.

(5) P. S. Skell and L. D. Wescott, *J. Am. Chem. Soc.*, **85**, 1023 (1963).

(5a) NOTE ADDED IN PROOF. Skell and Engel [*ibid.*, **87**, 1135 (1965)] have just reported the reaction of C₁ from a carbon arc with *cis*- and *trans*-2-butenes.

to investigate the reactions of hot and moderated carbon atoms with organic substrates.⁶ Hot carbon atoms have been found to react with benzene to form radioactively labeled toluene.⁷ Accelerated carbon ions, C⁺, with kinetic energies as low as 45 e.v., have been shown by Mullen to react with benzene to form both toluene and cycloheptatriene.⁸ Our results provide the first demonstration of a reaction between an organic substrate and carbon atoms produced with an initial kinetic energy below 0.3 e.v.

Methylene produced by the photolysis of diazomethane reacts with benzene to give toluene and cycloheptatriene.⁹ It is attractive to visualize carbene-like insertion and addition steps in the reactions of carbon atoms with benzene. Indeed, Wolfgang has postulated^{6b} and demonstrated^{6b} insertion by carbon atoms into C-H and ethylenic double bonds. However, we cannot say where, along the reaction pathways leading to toluene and cycloheptatriene, do the necessary hydrogen abstractions take place. Also, we cannot yet offer a proven explanation for the elimination of the toluene and cycloheptatriene yields and for the formation of the dark brown nonvolatile material when too much carbon (>400 μ g.) is deposited in the bombardments.

(6) (a) See review by A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 201 (1964); (b) M. Marshall, C. MacKay, and R. Wolfgang, *J. Am. Chem. Soc.*, **86**, 4741 (1964); J. Dubrin, C. MacKay, and R. Wolfgang, *ibid.*, **86**, 4747 (1964), and references cited in these articles.

(7) A. P. Wolf, *Rec. trav. chim.*, **80**, 533 (1961).

(8) R. Lemmon, R. T. Mullen, and F. L. Reynolds, in "Chemical Effects of Nuclear Transformation," Vol. II, International Atomic Energy Agency, Vienna, 1961, pp. 27-35.

(9) *E.g.*, (a) W. E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **75**, 297 (1953); (b) G. A. Russell and D. G. Hendry, *J. Org. Chem.*, **28**, 1933 (1963).

Jeremy L. Sprung, S. Winstein, W. F. Libby

Contribution No. 1802 from the Department of Chemistry
University of California, Los Angeles, California 90024

Received February 24, 1965

On the 260 m μ Cotton Effect in L-Phenylalanine¹

Sir:

Of late there has been disagreement among several workers²⁻⁵ as to the existence of a Cotton effect for the

(1) Financial support from the Alfred P. Sloan Foundation (A. M.), from NIH Grants HE-06314 and AMO5853-04, and from NSF Grant GP-825 is gratefully acknowledged.

(2) J. A. Schellman and C. G. Schellman, *Arch. Biochem. Biophys.*, **65**, 58 (1956).