± 15) kHz. Our result of $\chi_D = (176 \pm 15)$ kHz should be characteristic of a methyl group deuterium coupling constant, and it appears to be smaller than the calculated estimate of (210 ± 30) kHz which was obtained for DCH_3 using an extended basis-set LCAO–MO–SCF wave function for methane.[26] A more recent theoretical estimate of 175 kHz is cited for CD_4 by Pyykko and Pedersen[27] which is in good agreement with our result.

The magnetic susceptibility anisotropy in methylacetylene, given as $\chi_\perp - \chi_\parallel = (7.70 \pm 0.14) \times 10^{-6}$ erg/(G^2 mole), is only slightly larger than the value reported for $FC\equiv CH$ of[28] $\chi_\perp - \chi_\parallel = (5.19 \pm 0.12) \times 10^{-6}$ erg/(G^2 mole). These small anisotropies for $FC\equiv CH$ and $CH_3C\equiv CH$ are in sharp contrast to the large anisotropy estimated for the $-C\equiv CH$ group from proton chemical shift data.[29,30] Our results also seem to indicate that $\chi_\perp - \chi_\parallel$ in acetylene is considerably smaller than predicted by other estimates.[31]

The molecular quadrupole moment of $Q_\parallel = +(4.82 \pm 0.23) \times 10^{-26}$ esu cm^2 obtained here for methylacetylene is somewhat larger than the value of $+(3.96 \pm 0.14) \times 10^{-26}$ esu cm^2 found for fluoroacetylene.[28] The principal contributions to the molecular quadrupole moment come from the electrons in outer portions of the molecule. The CH bonds contribute positively to the value of $Q_\parallel$ in methylacetylene, thus indicating that electrons tend to be pulled in from the hydrogen nuclei toward the center of molecule.

It is also interesting to speculate on the nature of the additivity of the values of the second moment of the electronic charge distribution in molecules. The value of $\langle c^2 \rangle = (5.44 \pm 0.25) \times 10^{-16}$ cm^2 found here for methylacetylene is remarkably similar to the out-of-plane value of $\langle c^2 \rangle = (5.6 \pm 0.5) \times 10^{-16}$ cm^2 reported for acetaldehyde.[32] Both molecules have the same number of electrons and the same number of two protons out of the skeletal plane along the *b* axis in methylacetylene and the *c* axis in acetaldehyde. Previously we have suggested some simple rules for determining the value of the second moment of the electronic charge distribution perpendicular to the skeletal plane.[33,34] These rules are (1) one unit contribution for each first-row atom in the plane, (2) one-fourth unit contribution for each hydrogen atom in the plane, and (3) one unit contribution for each hydrogen atom out of plane.

Using these rules we can predict the value of $\langle c^2 \rangle$ in formic acid from the above result of $\langle c^2 \rangle = 5.6$ in acetaldehyde. Subtracting 2.0 for the two out of plane protons in acetaldehyde predicts $\langle c^2 \rangle = 5.6 - 2.0 = 3.6$ for formic acid which is in excellent agreement with the experimental value for formic acid of $\langle c^2 \rangle = (3.5 \pm 0.2) \times 10^{-16}$ cm^2 reported by Kukolich and Flygare.[35] Further examples of the validity of these simple rules are found in a discussion of linear molecules by Flygare, Shoemaker, and Hüttner.[36]

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged.

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Reactions of Accelerated Carbon Ions and Atoms with Benzene. Product Distribution as a Function of Charge and Kinetic Energy[1]

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Received January 2, 1969

Abstract: Monoenergetic beams of $^{14}C^+$ ions (from 15- to 0.1-keV kinetic energy), and beams of 5- and 0.5-keV carbon atoms, were allowed to impinge on a target of solid benzene at −196°. About 28% of the ions striking the benzene have been accounted for as identified C_2, C_6, C_7, C_8, C_{12}, and C_{13} hydrocarbons. The appearance of the known products was essentially unaffected by either the kinetic energy or the charge state of the impinging ions or atoms.

This report describes further efforts toward an understanding of the processes occurring when energetically "hot" carbon ions and atoms strike a benzene target. The principal interest in this subject was generated by the early reports that both recoiling carbon atoms, from the $^{14}N(n,p)^{14}C$ reaction,[2] and accelerated $^{14}C^+$ ions (KE = 5 keV)[3,4] lead to both benzene-^{14}C and toluene-^{14}C, the latter with about 15% of its radio-

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(1) Research sponsored by the U. S. Atomic Energy Commission.

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activity located in the ring.[4,5] Considerable strides have been made toward an understanding of the effects of recoiling carbon atoms on benzene through more recent work of Voigt,[6] Wolf,[7] Wolfgang,[8] and their collaborators. It is an intriguing problem to visualize how the new molecule of benzene-^{14}C is formed by interaction with the incoming ^{14}C atom or ion. Of equal interest is the understanding of the radioactivity distribution in the other major products (reported in the accompanying paper): toluene, cycloheptatriene, phenylcycloheptatriene, phenylacetylene, diphenylmethane, and biphenyl. The present paper reports product formation as a function of the charge state and the kinetic energy of the irradiating carbon ion or atom.

Experimental Section

Ion Accelerator. The carbon ion, and atom, accelerator used in this work has been described briefly.[4,9] Numerous recent modifications will be described in a forthcoming publication.

Irradiation Conditions. In the work reported here, an approximate 0.5–1.5 μA ($= 3$–9×10^{12} ions/sec) beam $^{14}C^+$ ions (monoenergetic), or a beam of C atoms (2×10^{12}/sec) (undetermined energy spread), at kinetic energies of 0.1–15 keV, was impinged upon a surface of solid benzene, at $-196°$, in the target chamber of the ion accelerator. The atomic beam was obtained by charge exchange on tungsten wire grids (1–2 mil ϕ, 10 mil spacing) followed by electrostatic separation of the residual ion beam. The solid benzene (at least 50 μ thick before the beam is turned on) was constantly added during an irradiation by the steady admittance of benzene vapor (Baker Analyzed reagent; further purified on a Carbowax glpc column). The ratio of incoming ions or atoms to benzene molecules in the target was about 10^{-4}. A 10-keV ion, therefore, deposits, on the average, 1 eV/molecule; this is equivalent to approximately 10^8 rads, a relatively high "radiation dose." The possibility of effects of radiation-damage products (fragments of benzene) on our final products cannot be excluded entirely. However, our data (see Table V), covering the dosage range between 0.01 and 1 eV/molecule, indicate that such effects are minimal. It appears that, in a system such as we are describing, most (probably 99.9%) of the ions' energy is lost in random fragmentations and interactions (including the pickup of H atoms) before the end of its track where it finally interacts with ground-state benzene to give labeled C_6, C_7, C_8, C_{12}, and C_{13} products.

Analytical Techniques. Following an irradiation, the solid benzene was scraped (under a dry N_2 atmosphere) into a rubber septum-stoppered flask, from which aliquot samples were withdrawn by syringe. (Volatile compounds, for example, acetylene (see below), are lost in this procedure.) Appropriate carrier amounts of known or suspected labeled products (such as toluene and cycloheptatriene) were added, and aliquot portions were analyzed by gas–liquid partition chromatography (glpc) on an instrument that recorded both mass (thermal conductivity cells) and radioactivity (proportional counter) detection. The initial chromatography was always done on a 0.25 in. × 11 ft column of 5% Carbowax 20M on DMCS-treated Chromosorb W (70–80 mesh); He flow rate 40 cc/min. The coincidence of carrier (mass) peaks and radioactivity peaks was taken as an indication of the molecular identity of the labeled material. Confirmations of identities were made by rechromatography on different substrates, and by the results of specific chemical reactions on the material appearing in the separately trapped peaks (see Table III). Details of the chromatography are described in the Ph.D. theses of Helmut Pohlit and Tz-Hong Lin, University of California, Berkeley, 1969.

To determine the radioactivity distribution in the benzene target, an aliquot of the target material was counted in a liquid scintillation counter. Another aliquot was injected into a glpc instrument, and the effluent trapped and counted, *i.e.*, not only the major peaks, but also whatever emerged between the peaks. The activity which remained on the first 10 cm of the column was recovered as follows. The normally empty injector tube was filled with the column substrate (20% Carbowax 20M on Chromosorb W), and after the emergence of the phenylcycloheptatriene this tube was removed from the glpc column and the contents emptied into a liquid scintillation counting vial for radioactivity determination. Finally, after reconnecting the glpc column, the activity emerging from the column during the 1 hr following the last major peak (phenylcycloheptatriene) was also trapped and counted.

Radiopurity of the Benzene and Cycloheptatriene. To make sure that no radioactive compounds were being masked in the large benzene peak, this peak was trapped from the glpc into *n*-pentane; one aliquot was rechromatographed and its specific activity determined. Another aliquot was hydrogenated in *n*-pentane over PtO_2 for 1 hr at 23° and 1.5 atm of H_2. The sample was purified again on glpc and trapped, and the specific activity was determined. A third aliquot was treated with bromine and rechromatographed and the specific activity checked again. The data in Table I show that within the limits of experimental error (*ca.* ±1.5%) the ^{14}C activity in the benzene peak area is indeed due to benzene-^{14}C.

Table I. Radiopurity of Benzene

Sample	Expt no.	Weight, mg	Specific activity, dpm/mg × 10^{-3}
Inject aliquots of *n*-pentane	1	4.627	1.95
solution, trap benzene-^{14}C	2	4.120	2.01
	3	3.077	1.93
Hydrogenation		2.126	1.93
Bromination	1	4.304	1.93
	2[a]	1.430	1.96

[a] Here the trapped benzene was reinjected and retrapped in order to eliminate some background mass contamination which appeared in the first run.

A similar type of check was made on the "CHT" peak area. The specific activity of cycloheptatriene-^{14}C (CHT), as trapped from the glpc, was compared with that of its Diels–Alder adduct with dimethyl acetylenedicarboxylate (see Table II).

Table II. Radiopurity of Cycloheptatriene

Sample	Expt no.	Weight, mg	Specific activity, dpm/mole × 10^8
Inject aliquots of *n*-pentane	1	1.763	1.61
solution of CHT-^{14}C; trap	2	2.822	1.61
CHT	3	2.943	1.60
Diels–Alder adduct[a]	1	0.975	1.53
	2	2.035	1.53

[a] Dimethyl acetylenedicarboxylate (prepared as in ref 10).

Results

Products Identified. Coincidence of glpc radioactivity and mass tracings from an aliquot of the target to which, after irradiation, carrier compounds were added, permitted definite identification of the following labeled products (in addition to benzene): toluene, cycloheptatriene, phenylacetylene, biphenyl, diphenylmethane, and phenylcycloheptatriene. Phenylhexane was also used as a "carrier" for an as yet unidentified compound ("U-2"; see below). These identifications were made completely secure by further cochromatog-

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raphy, both before and after specific chemical reactions (see Table III).

Table III. Results of Specific Chemical Reactions on the Eight Major Compounds Obtained from ^{14}C-Benzene Interactions

Compound	Reaction	Product
Benzene	Hydrogenation[a]	Unchanged
Toluene	$KMnO_4$ oxidn	Benzoic acid
	Hydrogenation[a]	Unchanged
CHT	Hydrogenation[a]	Cycloheptane
$PhC{\equiv}CH$	Hydrogenation[a]	$PhCH_2CH_3$
U-2	Hydrogenation[a]	Toluene Methylcyclohexane
Biphenyl	CrO_3 oxidn	Benzoic acid
	Hydrogenation[a]	Unchanged
Ph_2CH_2	SeO_2 oxidn	Ph_2CO
	Hydrogenation[a]	Unchanged
PhCHT	Hydrogenation[a]	Phenylcycloheptane

[a] Over PtO_2 for 1 hr at ambient temperature; 2 atm of H_2.

Earlier unpublished work in this laboratory[11] led to the identification of the following products, all of which emerged from the glpc columns before (lower retention times than) benzene: allene, propyne, 1,2-butadiene, 1,-3-butadiene, and 1-butyne. Only rough estimations of yields were made; however, all five of these products were produced with yields below 0.1%.

Work during the refereeing of this manuscript has shown that labeled acetylene is also a prominent product (yield of the order of 5%) of our system. The acetylene was observed after vacuum transfer of the target material, in contrast to our usual solid-transfer technique.

Glpc tracings were also made of an aliquot of the target benzene (plus carriers, as above) that was dissolved in *n*-pentane and hydrogenated, over PtO_2 for 1 hr at room temperature, under 2 atm of H_2. In addition to the hydrogenation products (listed in Table III), we have observed several other peaks and have preliminary evidence that these peaks are, at least in part, C_3–C_7 *n*-alkylbenzenes.

Summary of Radioactivity Distribution. Of all the ions that strike our benzene target, we have been able to account for about 88% of them on our glpc traces, and about 28% have been accounted for as identified, labeled compounds. Table IV summarizes this accounting.

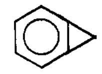
Search for Other Labeled Products. The following compounds were specifically sought as possible labeled products resulting from the interaction of $^{14}C^+$ ions with solid benzene: benzocyclopropene,[12] cyclooctatetraene,[13] 2-phenyltoluene,[14] methylcycloheptatriene,[15] styrene, and bicyclo[2.2.1]heptadiene-2,5.[16] These compounds, if they are products of the system under study here, are produced in yields below 0.3%.

Table IV. ^{14}C Activity Distribution Observed in Glpc Columns

Area trapped from glpc	% of total activity injected
Pre-benzene	0.4[a]
Benzene	3.8
Benzene to toluene	0.8
Toluene	1.8
CHT	4.3
CHT to phenylacetylene	3.2
Phenylacetylene	2.2
Phenylacetylene to U-2	0.6
U-2	2.7
U-2 to biphenyl	8.0
Biphenyl	1.5
Diphenylmethane	2.5
PhCHT	6.4
Emerging from glpc during succeeding hr (at 250°)	7.0
Remaining in injector filling	37.4
Total	82.6

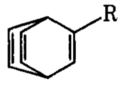
[a] This value ignores volatile products, such as acetylene (about 5% yield, see above) that was observed with a vacuum-transfer procedure.

The C_7 hydrocarbon benzocyclopropene



was regarded as a likely candidate for our unknown compound, U-2. This compound is also rather unstable, as indicated by its partial (about 10%) conversion into other compounds during rechromatography. That U-2 is a C_7 compound is indicated by our results showing that all the radioactivity (within experimental error) of U-2 appears on hydrogenation as toluene and methylcyclohexane. However, benzocyclopropene proved to be not identical (by cochromatography) with the U-2, neither did it coincide with any of the other recognizable radioactive peaks on our chromatograms. It appears that U-2's glpc retention times do not fit any known C_7 hydrocarbon. Indeed, it is possible that U-2 is not a hydrocarbon since our reactive system is exposed to the vacuum-tank atmosphere.

Mechanistic considerations led us to search for some additional possible products, such as



R = H, CH_3, or C_6H_5

These compounds were available to us only in their fully saturated forms, and we therefore sought them in the hydrogenated irradiation sample. Our data set an upper limit to the possible yield of the two compounds where R = H (bicyclo[2.2.2]octane) and R = CH_3 of 5×10^{-4}%. The phenyl analog appeared in a yield of approximately 0.05%.

The spiro[6.6]tridecane[17] was also sought in our hydrogenated target material. This is the saturated analog of spiro[6.6]tridecahexaene, which is a likely

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(11) R. T. Mullen, "The Chemical Interaction of Accelerated Carbon-14 Ions with Benzene" (Ph.D. Thesis), Lawrence Radiation Laboratory Report No. UCRL-9603, March 1961.

(12) Kindly provided by Professor E. Vogel, Institut für Organische Chemie der Universität, Köln, Germany.

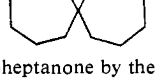
(13) Obtained from the J. T. Baker Chemical Co.

(14) Prepared following the procedure of I. R. Sherwood, W. F. Short, and R. Stansfield, *J. Chem. Soc.*, 1832 (1932).

(15) Prepared from toluene and CH_2N_2 over CuBr; after thermal isomerization all four of the methyl isomers were obtained.

(16) Obtained from Matheson Coleman and Bell, East Rutherford, N. J.

(17) This compound's structure is



It was prepared from cycloheptanone by the procedure given in *Compt. Rend.*, **239**, 1805 (1954).

Table V. Effect of Charge and Energy on the Incorporation of ^{14}C into Products

Energy and charge state[a]	% yields, based on total activity in target							
	Benzene	Toluene	CHT	PhC≡CH	U-2	Biphenyl	Ph_2CH_2	PhCHT
15 keV $^{14}C^+$ ion	3.6 ± 0.2	1.5 ± 0.3	4.1 ± 0.2	2.0 ± 0.2	2.4 ± 0.3	1.3 ± 0.2	2.3 ± 0.2	5.8 ± 0.6
5 keV $^{14}C^+$ ion	4.2 ± 0.2	1.3 ± 0.1	3.3 ± 0.2	2.1 ± 0.1	3.4 ± 0.2	—	2.4 ± 0.4	6.3 ± 0.3
5 keV spread $^{14}C^+$ ion beam	4.4 ± 0.2	1.5 ± 0.1	3.3 ± 0.2	2.1 ± 0.1	3.4 ± 0.2	2.1 ± 0.1	2.3 ± 0.1	6.0 ± 0.2
5 keV ^{14}C atoms	3.4 ± 0.4	1.0 ± 0.1	2.5 ± 0.3	1.6 ± 0.4	2.6 ± 0.8	1.3 ± 0.2	1.5 ± 0.1	5.3 ± 1.8
1.5 keV $^{14}C^+$ ion	5.7 ± 0.2	1.3 ± 0.1	2.9 ± 0.1	2.3 ± 0.2	4.1 ± 0.3	2.3 ± 0.6	2.5 ± 0.4	5.5 ± 0.4
0.5 keV $^{14}C^+$ ion	4.8 ± 0.2	1.0 ± 0.1	2.3 ± 0.1	2.2 ± 0.1	5.1 ± 0.3	1.7 ± 0.2	2.8 ± 0.1	6.0 ± 0.2
0.5 keV ^{14}C atoms	3.7 ± 0.2	0.9 ± 0.1	1.8 ± 0.1	1.9 ± 0.1	5.5 ± 0.1	2.5 ± 0.1	1.9 ± 0.3	5.5 ± 0.5
0.1 keV $^{14}C^+$ ion	5.7 ± 0.2	1.1 ± 0.1	2.2 ± 0.1	3.1 ± 0.1	8.3 ± 0.5	2.9 ± 0.5	3.8 ± 0.1	6.6 ± 0.2

[a] We estimate that the figures for the energies of the ion and atom beams are accurate within ±5%. The energy *spread* is 2–5 eV in the ion beam (M. von Ardenne, "Tabellen zur Angewandten Physik," Band 1, VEB Deutscher Verlag der Wissenschaften, Berlin, 1962, p 651). The energy spread in the atom beam is probably not much larger since (1) scattering of low-energy ions on metal surfaces can be considered as occurring between free atomic systems (B. V. Panin, *Soviet Phys. JETP* (English Transl.), **15**, 215 (1962)), and (2) charge transfer is associated with small-angle scattering, *i.e.*, small losses of kinetic energy (S. K. Allison and M. Garcia-Munoz, "Atomic and Molecular Processes, Academic Press, New York, N. Y., 1962, p 721).

product of the interaction of an energy-rich seven-carbon species (benzene + the single-carbon ion or atom of the beam) with a neighboring benzene molecule. However, the spiro compound, if it is formed at all, would account for less than 0.05% of the carbon ions striking the benzene.

Effect of Charge State on Product Distribution. Table V shows the measured yields (in per cent of irradiating ^{14}C ions or atoms) of the various products for 15-, 5-, 1.5-, 0.5-, and 0.1-keV ions, and 5- and 0.5-keV atoms. It also shows the results when a 5-keV $^{14}C^+$ beam, which is usually about 2 mm in diameter, was spread to cover a 2-cm diameter area. The figures are the averages of between two and five separate determinations on aliquot portions. In the case of the 5-keV atom figures, two separate irradiations were made.

Discussion

Dependence on Irradiation Conditions. With the exception of one product, U-2, the data of Table V show an insensitivity, in the amounts and kinds of products formed, to either the charge state or the kinetic energy of the irradiating particle. This was expected for the following reasons. (a) The large cross-section for electron capture[18,19] achieves neutralization of the carbon ion (upon penetration of the benzene matrix) during the first few energy-degrading quasi-elastic collisions. After that, recurrence of charged states is, according to the resonance rule,[20] highly improbable. The bond-forming species is therefore always a neutral carbon atom.[21] (b) Chemical bond formation is not expected at energies above 50 eV. Kinetic theory leads us to expect, therefore, that the yields and kinds of products are independent of the initial energy of the irradiating particle as long as it is larger than 100 eV. This is because the collision probability below a certain energy E_0 is the same for all particles with initial energy above approximately $2E_0$.[22] Our results so far are in accordance with this interpretation.

The increase in yield of U-2 by about a factor of 3 as the energy decreases to 100 eV is hard to explain. The yield increase is probably connected with the lower total production of benzene debris since this is the only quantity expected to change drastically, *i.e.*, approximately proportional to the beam energy. It is possible that U-2 is sensitive to the amount of debris *via* reaction with some component(s) thereof after liquefaction of the irradiation sample.

That "radiation damage" is of little importance in our analysis (except for U-2) is indicated by the fact that a 150-fold change in the total energy dose delivered to the benzene target (the 15-keV *vs.* the 0.1-keV data of Table V) results in little difference in product yields. Furthermore, at no energy of the incoming ^{14}C do we see much evidence of ^{14}C reacting with benzene fragments; that is, there is little activity in products with a lower molecular weight than benzene (see Table IV).

Mechanisms. We know the final products for only about one-fourth of the ions that strike the target. Although we can say little about the other three-quarters, we can attempt to outline the chemical transformations leading to the seven identified major products. The structures of some of these products (one C_6, two C_7, one C_8, one C_{12}, and two C_{13} hydrocarbons) are quite suggestive with respect to the mechanisms possibly involved. Similarities to, particularly photo- (but also thermal) chemistry, make it plausible to assume that cycloheptatriene and toluene are products of methylene (formed from carbon by pickup of hydrogens), while diphenylmethane and phenylcycloheptatriene (empirical formula = two benzene + one C) may well arise from the reaction of a bare carbon with two benzene molecules. Phenylacetylene may be due to C_2 precursors. We can speculate with even less justification about the formation of benzene, U-2, and biphenyl, due to the absence of any reasonable comparison with thermal chemistry. An appraisal of the possible mechanisms is the subject of the following paper.

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