The forward and reverse of reaction 3 were each studied at 15.0° and 0.100 M ionic strength. Concentrations were adjusted in an attempt to permit the two directions of reaction to be studied independently of one another.[5] The oxidation of $[Ta_6Cl_{12}]^{3+}$ by iron(III) follows the rate equation

$$d[Fe^{2+}]/dt = k_{34}[[TaCl_{12}]^{3+}][Fe^{3+}] \qquad (6)$$

with $k_{34} = 3.72\ M^{-1}\,sec^{-1}$ (±0.31, standard deviation in 10 runs). These studies covered the concentration range 0.0015–0.010 M iron(III). The rate law for the reaction of $[Ta_6Cl_{12}]^{4+}$ and iron(II) is

$$-d[Fe^{2+}]/dt = k_{43}[[Ta_6Cl_{12}]^{4+}][Fe^{2+}] \qquad (7)$$

with $k_{43} = 201\ M^{-1}\ sec^{-1}$ (±10, standard deviation in 10 runs). Initial iron(II) concentrations lay in the range 10^{-5}–$10^{-3}\ M$.

These data lead to a value for the equilibrium quotient of reaction 3, $Q_{34} = k_{34}/k_{43} = 0.018$ (±0.0025 standard deviation) at 15.0° and 0.100 M ionic strength. The equilibrium was also studied directly by spectrophotometry at 8100 A, where $[Ta_6Cl_{12}]^{3+}$ absorbs 3.4 times more intensely than does $[Ta_6Cl_{12}]^{4+}$. In four experiments covering 6–60% as the oxidized complex, we found $Q_{34} = 0.016 \pm 0.002$ at 0.100 M ionic strength and room temperature (22 ± 2°).

An attempt was made to study the rate of reaction of $[Ta_6Cl_{12}]^{2+}$ and $[Ta_6Cl_{12}]^{4+}$ (reaction 4), but in every instance the reaction was apparently complete upon mixing. In a run $3 \times 10^{-5}\ M$ in each cluster ion, the first reading was taken 5 sec after mixing and indicated the reaction was >95% complete in this time; assuming a simple mixed-second-order rate law, a lower limit was placed that $k > 1 \times 10^5\ M^{-1}\,sec^{-1}$.

Apparently, simple bimolecular reaction mechanisms account satisfactorily for the reactions studied here, where second-order kinetics always were observed. No evidence was found for any complexities, such as reaction intermediates or hydrogen ion dependences. The reactions are quite rapid, which is consistent with the relative lack of molecular rearrangement accompanying electron transfer.

A study of the stoichiometry, kinetics, and mechanisms of electron-transfer reactions of these tantalum cluster complexes promises to provide some interesting results on these novel substances.

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(5) In the two series of experiments performed here, reduction of $[Ta_6Cl_{12}]^{4+}$ by iron(II) was calculated to be between 88 and 99.98% complete, and oxidation of $[Ta_6Cl_{12}]^{3+}$ by iron(III) between 78 and 95% complete. In this preliminary treatment of data, failure of the reactions to run to completion was ignored. A number of additional runs on the reaction of $[Ta_6Cl_{12}]^{3+}$ and iron(III), where the extent of equilibrium conversion was somewhat lower, are not reported here.

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Reaction of Free Carbon Atoms with Cyclopentadiene

Sir:

We have studied the interaction of free carbon atoms with gaseous cyclopentadiene. This system is of special interest in the development of a general mechanism for reactions of atomic carbon in organic systems.[1] Rearrangement and/or decomposition of the adducts ($C + C_5H_6$) formed can be predicted with an unusual degree of confidence, with only relatively few final products being expected to be formed in major yield. For this reason, the system provides an excellent test of our understanding of the fundamental mechanisms of carbon atom reactions. In addition, results provide a basis for comparison in attempting to understand the difficult problem of reaction of carbon with benzene.

Free carbon atoms were produced in the form of C^{11} (20.5 min) by nuclear techniques described in detail elsewhere.[1,2] Such atoms are expected, on the basis of certain theoretical considerations,[1c,3] to be in low-lying electronic states (^3P, ^1D, ^1S), an expectation consistent with all results obtained. Their reactions were studied both in unmoderated systems, in which products may be formed in "hot" reaction, and in mixtures moderated by sufficient neon so that virtually all the atoms reacted "thermally," *i.e.*, after removal of their excess kinetic energy.[4]

Table I.[a] Yields of C^{11}-Labeled Products from Reactions of C^{11} with Cyclopentadiene

Product	Hot system cyclopentadiene (30.0 cm)	Thermal system cyclopentadiene (4 cm)–neon (76 cm)
Carbon monoxide[b]	0.7 ± 0.3	1.6 ± 0.1
Acetylene	10.0 ± 1.0	2.9 ± 0.1
Vinylacetylene	3.8 ± 0.1	2.2 ± 0.1
Diacetylene	8.9 ± 0.3	3.2 ± 0.1
Bicyclo[1.3.0]hexene-3[c]	1.2 ± 0.3	<0.2
Fulvene[d]	3.0[d]	1.2[d]
Benzene	8.6 ± 0.3	11.2 ± 0.5
cis-1,3-Hexadien-5-yne	2.1 ± 0.2	5.2 ± 0.8
trans-1,3-Hexadien-5-yne	1.2 ± 0.1	3.3 ± 0.4
Low mol wt minor products	2.0	Not detn
Polymer[e]	59 ± 5.0	70 ± 5.0

[a] All yields given in per cent absolute activity. Total volatile activity for unmoderated sample is about 55%, for moderated sample 35%. (This includes unidentified but volatile material classified as "polymer." See footnote *e* below.) [b] Results from reaction with oxygen impurity. [c] Probably results from reaction of CH_2 with cyclopentadiene. [d] Both the hot and thermal yields reported here are for samples with oxygen scavenger present and with a C_5H_6:O_2 ratio of 19:1. We believe that these are the significant yields for fulvene. In the absence of oxygen, fulvene is difficult to recover and yields are erratic. Apparently fulvene is particularly susceptible to destruction by reaction with radicals produced in the radiation field. Oxygen scavenges such radicals efficiently and permits recovery of fulvene. [e] Represents polymer, defined here as material containing more than six carbon atoms.

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(1) For recent reviews, see (a) C. MacKay and R. L. Wolfgang, *Science*, **148**, 899 (1965); (b) A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 210 (1964); (c) R. L. Wolfgang, *Progr. Reaction Kinetics*, 3, 99 (1965).

(2) J. Durbin, C. MacKay, M. L. Pandow, and R. L. Wolfgang, *J. Inorg. Nucl. Chem.*, **26**, 2113 (1964). Experimental details were largely as described in this work and in ref 5.

(3) M. Marshall, C. MacKay, and R. L. Wolfgang, *J. Am. Chem. Soc.*, **86**, 4741 (1964).

(4) The results of the experiments with neon moderation indicate that even at 95% moderation hot reactions play a minor role in determining the product spectrum. At this concentration, the sum yield

Of the order of 10^8 atoms of C^{11} were produced in each run. Analysis of those products incorporating C^{11} atoms was by the usual radio gas chromatographic methods.[1,2] Results are shown in Table I. It is seen that a relatively few specific products plus polymer make up the bulk of the yield. None of ten other volatile products found has an individual yield greater than 0.3%. It is interesting to note that this system presents a method for relatively efficient aromatic synthesis of benzene.

The major mechanisms of reaction of atomic carbon with hydrocarbons have been shown to be insertion into C—H and C═C bonds.[1,3,5] The adducts expected on this basis are I, II, III, and IV in Figure 1. They may be either triplet or singlet depending on the multiplicity of the carbon forming them; however, for the sake of brevity and because it does not affect our primary conclusions, we do not make this distinction here.

These adducts may form final products by isomerization involving an H-atom shift. However, even when formed by thermal carbon, they will be quite excited and unless rapidly deactivated will tend to decompose. The path of such decomposition is then predicted by the usual criteria. Modes in which there is a stable "leaving group" are favored, this being equivalent to the requirement that the over-all reactions have high exoergicity, thus tending to maximize the number of states in product phase space which are available. Furthermore, reactions requiring extensive or unusual internal rearrangements are excluded.

It is seen that there is a remarkable correspondence between the results in Table I and the expectations of the model as summarized in Figure 1. Not a single product of appreciable yield is expected but not observed, or observed but not expected.[6] Furthermore, the trends in yield with changes of experimental parameters are as expected. For instance, on going from hot to thermalized carbon atoms and thus to less-excited adducts, the total yields of products formed by extensive fragmentation, acetylene, diacetylene, and vinylacetylene, drop from two-thirds to one-third of the volatile activity. Simultaneously, there is noted a corresponding increase in the total yield of products of relatively low-energy processes, such as benzene and 1,3-hexadien-5-ynes.

Other experimental parameters, such as dependence on phase and oxygen scavenger, provide further detail on the reaction model. This discussion will be provided in the full paper to follow. For the present, however, it is clear that the previously postulated mechanisms are a successful and specific description of the present system.

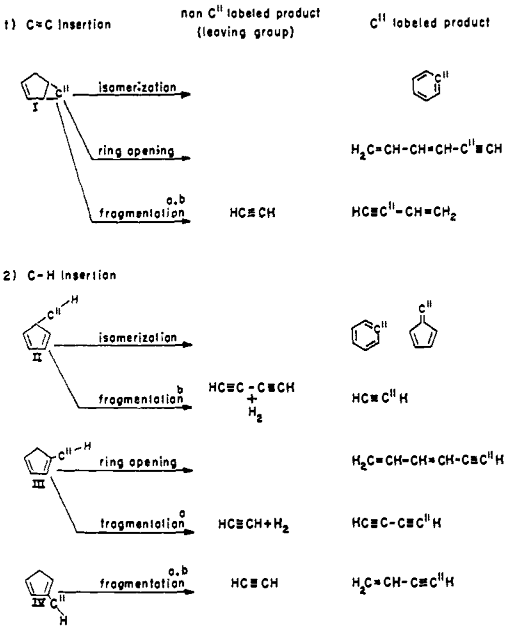

Figure 1. Expected major mechanism of reaction of postulated adducts formed by C-atom insertion into C═C and C—H bonds of cyclopentadiene. For reasons of space, not all possible mechanisms fulfilling the criteria given in the text can be included, but these also lead to the same products. (a) Other fragmentation processes accompanied by H-atom shifts can lead to acetylene-C^{11}. (b) Other fragmentation processes accompanied by H_2 elimination can lead to diacetylene-C^{11}.

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of the major fragmentation products is 8% as compared to 25% in an unmoderated system. Even more significant is the behavior on going from 95 to 99% moderation. Over this range, the amount of reactant, and, to a first approximation, the number of hot collisions and reaction, are reduced fivefold. Yet the sum yield of fragmentation products decreases by only 10%. Hence it would appear that even at 95% neon moderation, the results are little perturbed by hot reaction. The yields of benzene actually drop as one proceeds from 95 to 99% moderation. However, since the yield passes through a maximum as the neon concentration is increased, other effects in addition to translational energy moderation must be important.

(5) J. Dubrin, C. MacKay, and R. L. Wolfgang, *J. Am. Chem. Soc.*, **86**, 4747 (1964).

(6) The mechanism of polymer formation is not explicitly discussed here. There are are many plausible modes by which the adducts can react with further molecules of cyclopentadiene. In the absence of specific information on the makeup of the polymer, it is not appropriate to examine such addition modes in detail.

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Evidence for the Formation and Reaction of Methyne

Sir:

We wish to report on the apparent production of methyne (CH) by reaction of free carbon atoms with hydrogen, and on its reaction with ethylene.[1] Atomic carbon in the form of translationally excited (hot) C^{11} was produced in mixtures of H_2 and C_2H_4 employing nuclear techniques now standard.[5,6] Analysis of products was by radio gas chromatography using the 20.5-min activity to assay the yield of each C^{11}-labeled

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(1) The reaction with ammonia of CH produced in flames has been reported.[2] Methyne has been postulated as a possible intermediate accounting for the formation of ethylene in the reaction of atomic carbon with saturated hydrocarbons.[3,4] This product can also be accounted for by direct reaction of C atoms, and, as yet, it is uncertain which species is actually involved.

(2) D. R. Safrany, R. R. Reeves, and P. Harteck, *J. Am. Chem. Soc.*, **86**, 3160 (1964).

(3) (a) A. P. Wolf, *Advan. Phys. Org. Chem.*, **2**, 210 (1964); (b) A. P. Wolf and G. Stöcklin, Abstracts, 146th National Meeting of the American Chemical Society, Denver, Colo., Jan 1964, p 32C.

(4) D. E. Clark and A. F. Voigt, *J. Am. Chem. Soc.*, **87**, 5558 (1965).

(5) J. Dubrin, C. MacKay, M. L. Pandow, and R. L. Wolfgang, *J. Inorg. Nucl. Chem.*, **26**, 2113 (1964).

(6) J. Dubrin, C. MacKay, and R. L. Wolfgang, *J. Am. Chem. Soc.*, **86**, 4747 (1964).