viously measured, we have no basis on which to compare our values directly. Neither set of values for either mathematical treatment appears, from existing information, to be entirely unreasonable.

The values of k were found to be statistically identical within 99.5% confidence level, and assuming that $K = \infty$, the theoretical maximum amount of heat which could be obtained was calculated and is plotted in Figure 4 along with the experimental points. The values beyond the 1:1 molar ratio when sodium dodecyl sulfate is held constant are too high, and this can possibly be explained as the reaction of the excess cationic detergent with the glass reaction vessels as reported by Blackman and Harrop.[17] When the concentration of cetylpyridinium chloride is held constant, the heat values are low owing to the 1 mole of water present for which no correction has been made. The remainder of the data fits our theoretical curve within experimental error.

Application of Calorimetry to Free-Energy Calculations. As an extension of the work of Benzinger[2] where he considered reactions of the type $A + B \rightleftharpoons C + D$, we have explored the reaction $A + B \rightleftharpoons C$. From experimentally measured heat values, thermodynamic parameters have been calculated. The application of calorimetry to this type of system can be a valuable tool in the investigation of other similar systems. Calorimetrically, this could represent a model for many important biological reactions such as antigen–antibody, hemoglobin–haptoglobin, and avidin–biotin.

Acknowledgments. The authors are grateful to Dr. C. L. Sutula for his many helpful suggestions.

(17) L. C. F. Blackman and R. Harrop, *J. Appl. Chem.*, 18, 43 (1968).

Formation of Excited Intermediates in Recoil Carbon Atom Reactions. Pressure-Dependence Studies in the Gas Phase[1]

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Contribution from the Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973. *Received May 13, 1969*

Abstract: The variation in yield of carbon monoxide-C^{11}, acetylene-C^{11}, and ethylene-C^{11} from the reaction of recoil carbon atoms with methane, propane, cyclopropane, and neopentane has been studied as a function of the hydrocarbon gas pressure. The hydrocarbons contained 4.5% added oxygen as scavenger. The total gas pressure was varied over a 1000-fold range in all cases except neopentane where the pressure range was varied 100-fold. In all cases studied the yield of carbon monoxide-C^{11} decreased with increasing pressure and yields of acetylene-C^{11} and ethylene-C^{11} increased with increasing pressure. A model is presented which invokes a collision complex being formed prior to carbene formation where the excited carbene then can fragment or react further to give the observed products. The nature of the collision complex is suggested as being responsible for the observed pressure dependency.

The reaction of energetic carbon atoms with hydrocarbons produces acetylene and often ethylene in high yields. Upon addition of oxygen scavenger, carbon monoxide is also formed because the carbon atoms which reach thermal energies react preferentially with oxygen.[2,3] The mechanisms currently proposed for the reaction of carbon atoms involve insertion of either carbon atoms,[4] methyne,[2a,c] or methylene[2a,c] to form excited intermediates. Since phase-effect studies have shown that such intermediates can be stabilized in a solid or liquid matrix,[5,6] pressure-dependence studies on the gas-phase reactions of carbon atoms were initiated[7] to investigate the single collisional deactivation of such intermediates, in systems where the environment of the attacking species is unaltered.[8] For recoil studies the $C^{12}(n,2n)C^{11}$, $N^{14}(p,\alpha)C^{11}$, $C^{12}(\gamma,n)C^{11}$, and $C^{12}(p,pn)C^{11}$ have been the most frequently used nuclear reactions. For pressure dependence studies the $C^{12}(p,pn)C^{11}$ reaction using the 1–3-GeV proton beam at the Brookhaven Cosmotron is ideal. This technique allows accurate monitoring of induced activity[2a,6] as well as low radiation damage to samples.

Experimental Section

Materials. Phillips Research Grade hydrocarbons were used after purification by freezing and melting on a vacuum line. Matheson reagent grade oxygen was used without further purification.

Irradiations. Irradiations were carried out using aluminum (2-S) vessels. All vessels were cylindrical with a 5-cm o.d.; the vessels varied in length from 1.25 to 20 cm. The vessel size used depended on the pressure of the sample. The vessel window thickness varied from 0.76 mm on the low-pressure vessels to 3 mm on the high-pressure vessels. The attenuation of the beam by the thick

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) G. Stöcklin and A. P. Wolf in "Chemical Effects of Nuclear Transformations," Vol. I, IAEA, Vienna, 1965, pp 121–132; (b) P. Lieberman, Ph.D. Thesis, City University of New York, New York, N. Y., 1967; (c) *cf.* A. P. Wolf, *Advan. Phys. Org. Chem.*, 2, 202 (1964).

(3) *Cf.* R. Wolfgang, *Progr. Reaction Kinetics*, 3, 99 (1965).

(4) C. MacKay, M. Pandow, P. Polak, and R. Wolfgang in "Chemical Effects of Nuclear Transformations," Vol. II, IAEA, Vienna, 1961, pp 17–26.

(5) C. E. Lang and A. F. Voigt, *J. Phys. Chem.*, 65, 1542 (1961).

(6) G. Stöcklin and A. P. Wolf, *J. Amer. Chem. Soc.*, 85, 229 (1963).

(7) H. J. Ache and A. P. Wolf, *ibid.*, 88, 888 (1966).

(8) In a pressure-dependence study the slowing down process of the attacking species is identical at low and high pressures and so the behavior of reaction intermediates can be examined. In mixed systems (*i.e.*, with inert gas added) not only may reaction intermediates be affected but also the energy distribution of the reacting species.

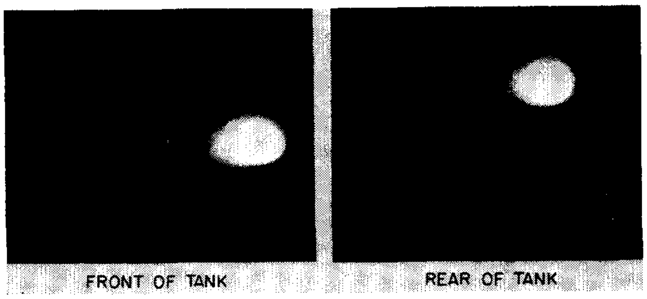

Figure 1. Polaroid photograph of 2-GeV proton beam traversing tank.

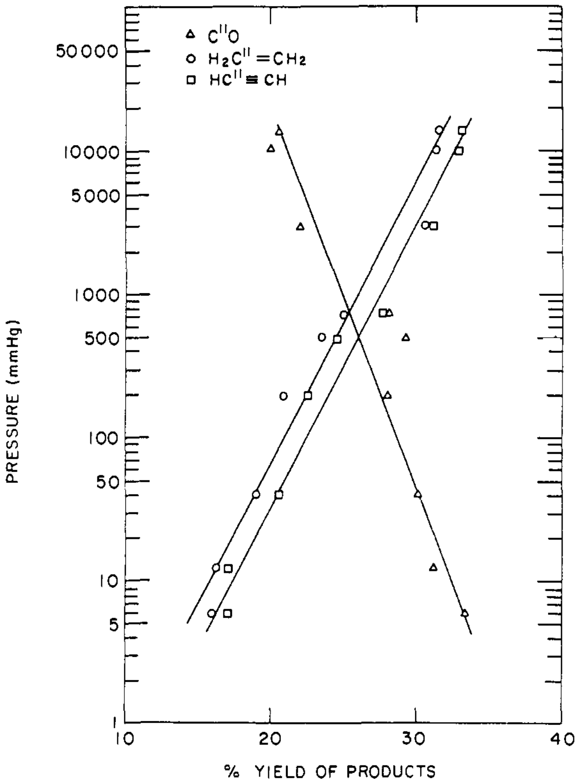

Figure 2. Pressure trend in oxygen-scavenged methane.

windows was negligible. All vessels were fitted with Circle Seal Type 9530-T-1 valves. Stainless steel taper joints were used so that the vessels could be fitted to the vacuum line. The high-pressure vessels were found to hold pressures of 10 atm for several days. Filling was performed by freezing known pressures of hydrocarbons (measured with a Statham Instrument, Model No. PA731TC-25-350 pressure transducer) from known volumes of the vacuum line, into the vessels. Oxygen was then allowed to expand into the vessels at known pressures. The composition of the samples was checked after irradiation by comparing the sizes of the oxygen and hydrocarbon peaks on the gas-chromatographic mass trace.

Polyethylene foils (0.01 mm) were fastened to each vessel to measure the total induced activity.[2a,6] Several samples were irradiated at once, the samples being held in line by an aluminum holder. The holder was aligned in the beam, and the alignment checked by exposing Polaroid film to one pulse of the beam. Figure 1 shows a typical final pair of pictures, showing the beam passing completely through the sample vessels. The samples were irradiated for 40 min to a total integrated flux of 1.7 × 10^{14} protons this flux producing an activity of ~50 nCi/mg of C. The radiation damage for such an irradiation was found by conventional acetylene–benzene dosimetry[9] to be ~10^{-5} eV/molecule. The radiation dose was independent of the window thickness of the irradiation vessel and of the position of a vessel in a series.

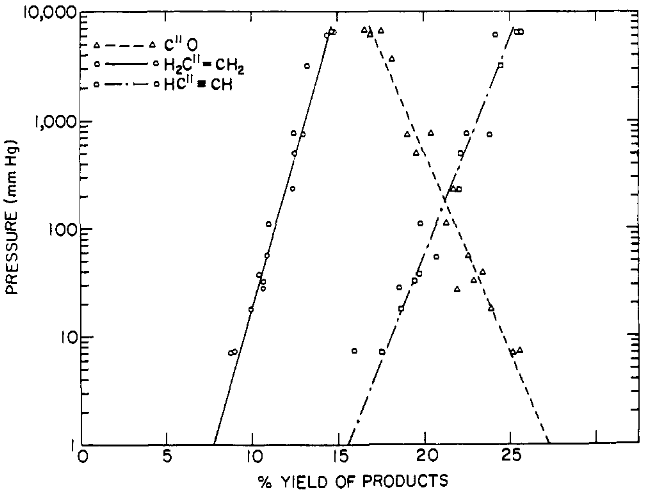

Figure 3. Pressure trend in oxygen-scavenged propane.

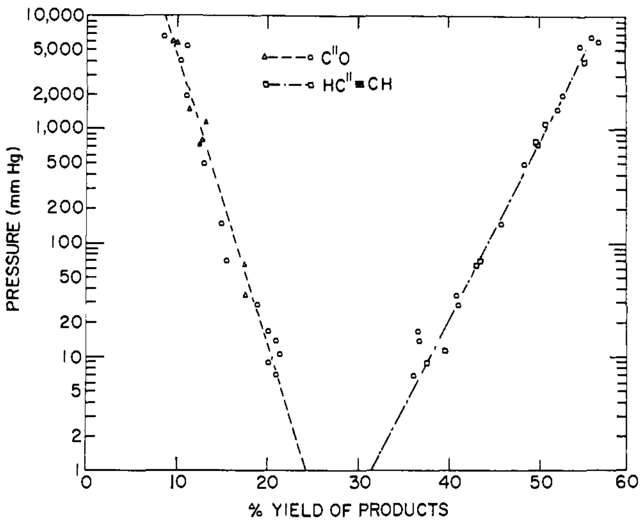

Figure 4. Pressure trend in oxygen-scavenged cyclopropane.

Analysis. The induced activity in the sample was measured by counting the middle foil of three polyethylene foils mounted on the vessels. A 4π-well counter was used. The loss of activity from the foil by diffusion was assumed to be 15%.[10]

After irradiation the sample vessel was fitted to a vacuum line. A measured portion of the sample was counted in a window-proportional counter of known efficiency[11] to give the total gas-phase activity. The other aliquots were passed through a gas–liquid partition chromatograph with an effluent stream counting system. This system is described in detail elsewhere.[12] It consisted of automatic injection devices, a multiple column gas chromatograph, hot-wire detector, cylindrical proportional flow counter,[13] recording flowmeter, and automatic data collection devices. The data were placed on paper tape or magnetic tape and computer evaluated. The columns used were: 2.4 m × 9 mm i.d. glass, containing 12% DC 350 Silicone oil on 60–80 mesh alumina; 1.8 m × 4 mm i.d. glass containing 60–80 mesh silica gel; 1.8 m × 4 mm i.d. glass containing Columbia Carbon Corp. 60–80 mesh activated charcoal.

Results

Five systems were investigated; methane, propane, cyclopropane, and neopentane all scavenged with 4.5%

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[9] *Cf.* F. Cacace and A. P. Wolf, *J. Amer. Chem. Soc.*, 87, 5301 (1965), and references therein.

[10] J. B. Cumming, A. M. Poskanzer, and J. Hudis, *Phys. Rev. Lett.*, 6, 484 (1961).

[11] D. R. Christman, Brookhaven National Laboratory Report No. BNL 50028 (T-445), 1966.

[12] M. J. Welch and A. P. Wolf, submitted for publication.

[13] M. J. Welch, R. Withnell, and A. P. Wolf, *Anal. Chem.*, 39, 275 (1967).

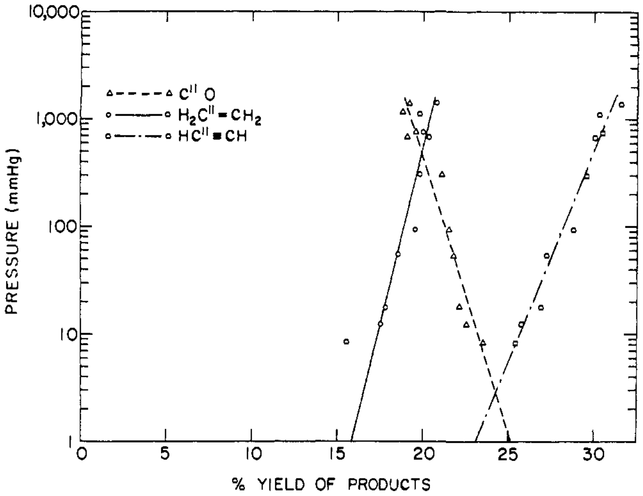


Figure 5. Pressure trend in oxygen-scavenged neopentane.

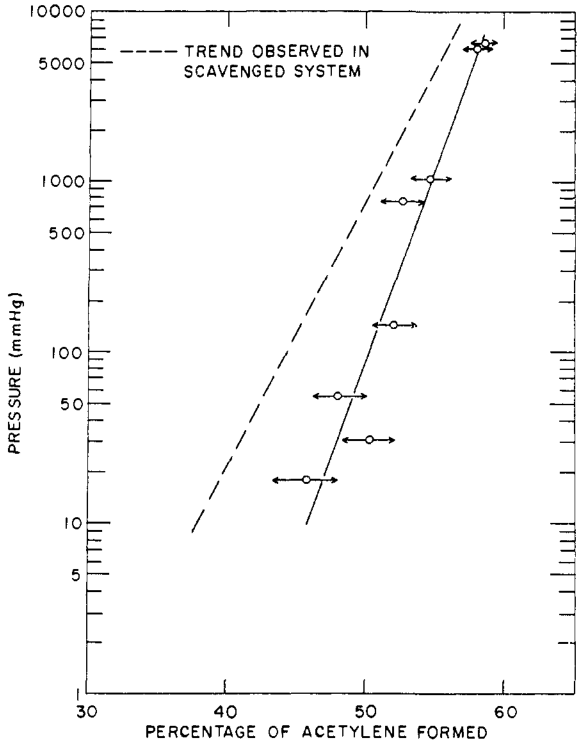


Figure 6. Pressure trend in unscavenged cyclopropane.

oxygen, and unscavenged cyclopropane. Figures 2–6 show the trends observed, while Figures 7 and 8 show the recoil loss at the various pressures used for propane and neopentane. The recoil-loss curves for the other systems were similar.

Because of the complexity of Figures 2–5, errors are shown only on Figure 6. The errors given here are, however, typical. At the higher gas pressures the samples analyzed can be large and so errors in the aliquot size and the counting rate are less than at low pressures. With the automatic flowmeter and computer data analysis, the errors in this work are lower than in previously published work. At high pressures the yields are generally ±3% and at the low pressures ±8%.

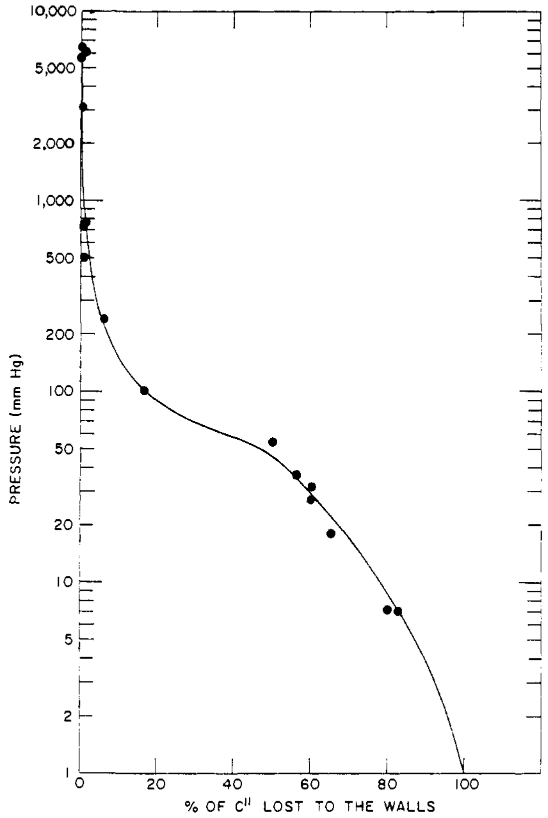


Figure 7. Recoil carbon-11 loss to walls in oxygen-scavenged propane.

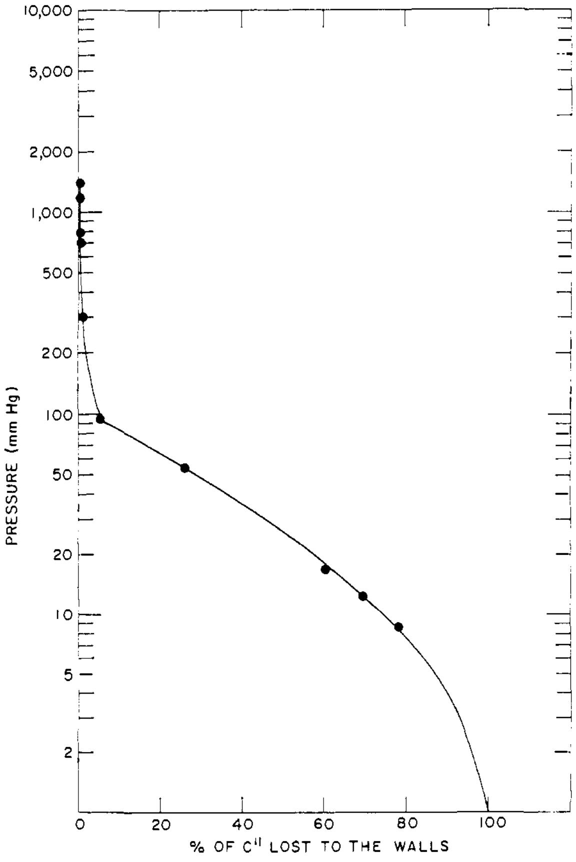
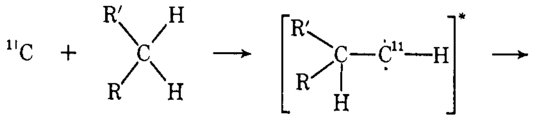


Figure 8. Recoil carbon-11 loss to walls in oxygen-scavenged neopentane.

Discussion

The four systems studied show similar pressure dependences, the hydrocarbon yield increasing and the carbon monoxide yield decreasing as the pressure is increased. It can be seen from the pressure-trend curves and the recoil-loss curves that the same pressure trends are observed in regions where the recoil loss is negligible, as in regions where the loss is high.

The current model[2c,3] for recoil carbon reactions is



products $[C_2H_2, \text{etc.}]$ (1)

shown in eq 1.[14] In order to accommodate this simple model to the observed pressure trends the excited carbene must be able to fragment (to moieties smaller than acetylene). The excited carbene must also be able to undergo collisional deexcitation and decompose to form acetylene, and allow the formation of ethylene and other products. The fragmentation products must react with oxygen to form carbon monoxide.

For this model to accommodate the observed pressure trends, the carbene intermediate must behave very differently from photochemically produced carbenes. In the case of photochemically produced cyclopropylcarbinyl carbene,[15] the acetylene yield shows no pressure dependence under the conditions studied while the acetylene yield from *trans*-1,2-dimethylcyclopropylcarbinyl carbene, also photochemically produced, decreases with increasing pressure under the conditions studied.[16] The ethylidine radical[17] can be stabilized by pressure, and the acetylene yield decreases with increasing pressure. It has also been found that isobutyl carbene and *n*-butyl carbene yield little or no acetylene at pressures comparable to those used in the present study.[18] Thus it can be seen that photochemically produced carbenes do not show the consistent behavior (relative to acetylene production) demonstrated for the "carbene" intermediates produced in the hot carbon atom reactions.

A further implication of the model is that its fragmentation products (*e.g.*, methyne, methylene, etc.) are readily oxidized to carbon monoxide. This is unlikely as methylene formed by other methods is known to form both carbon monoxide and carbon dioxide *via* oxidation by oxygen[19] while in the hot atom case carbon dioxide is a very minor product or is not found at all. Methyne has been shown to be reactive with simple hydrocarbons.[20] Consequently one would not expect methyne to react with the 4.5% of oxygen present in the pressure studies. The model currently proposed for energetic carbon atom reactions must therefore be modified in order to be consistent with the observed pressure trends.

The pressure trends observed can be accommodated by a model involving a collision complex as the first product yielding interaction between the energetic carbon atom and the substrate. The stabilization or dissociation of this complex leads to the observed pressure dependence.[21] It is possible to predict the type of pressure dependence expected from the model and to compare the predicted trends with the experimentally found trends. The modified model is given by the reaction sequence in eq 2[22] through 6.

$$C^{11}\neq + RH \xrightarrow{k_1} [C^{11}RH]^* \tag{2}$$

$$[C^{11}RH]^* \xrightarrow{k_2} [\text{carbene intermediates}]^* \tag{3}$$

$$[C^{11}RH]^* \xrightarrow{k_3} C(\text{thermalized}) + [RH]^* \tag{4}$$

$$[C^{11}RH]^* + RH \xrightarrow{k_4} [\text{carbene intermediates}]^* + [RH]^* \tag{5}$$

$$[\text{carbene intermediates}]^* \longrightarrow \text{hot products}^{23} \tag{6}$$

The following assumptions are made in developing the kinetic approach. (1) An energetic carbon–RH collision which can lead to products can also lead to a thermalized carbon atom. (2) Reactions of the type

$$[C^{11}RH]^* \longrightarrow C[\text{hot}] + RH^* \tag{4a}$$

can be ignored. That is to say that the hot carbon atoms produced in (4a) must in any event collide again with RH and undergo reactions 3, 4, or 5. (3) The step, [carbene intermediate]* → hot products (6), can show only a small pressure dependence in the systems studied.

As the concentration of RH is many orders of magnitude greater than the concentration of carbon atoms, a carbon atom must collide with a hydrocarbon and not with itself whatever the pressure. Since the proton flux was constant during all the runs made in the alkane systems, the rate of production of carbon-11 during any run was constant. If one assumes that the carbon atom can react with the substrate to form a complex with a probability p, then the over-all rate of change of $[C^{11}RH]^*$ is given by

$$\frac{d[C^{11}RH]^*}{dt} = p\frac{d[C^{11}]}{dt} - (k_2 + k_3)[C^{11}RH]^* + k_4[RH][C^{11}RH]^* \tag{7}$$

Assuming a steady-state concentration of $[C^{11}RH]^*$

$$[C^{11}RH]^* = \frac{p\dfrac{d[C^{11}]}{dt}}{(k_2 + k_3) + k_4[RH]} \tag{8}$$

Hot products are found *via* reactions given by eq 3 and 5; therefore, hot product formation can be given by eq 9 and 10, where HP equals hot product. As the total

$$\frac{d[HP]}{dt} = k_2[C^{11}RH]^* + k_4[C^{11}RH]^*[RH] \tag{9}$$

$$\frac{d[HP]}{dt} = \frac{(k_2 + k_4[RH])p\dfrac{d[C^{11}]}{dt}}{(k_2 + k_3) + k_4[RH]} \tag{10}$$

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(14) The asterisk implies excitation.

(15) P. B. Shevlin and A. P. Wolf, *J. Amer. Chem. Soc.*, 88, 4735 (1966).

(16) A. Guarino and A. P. Wolf, *Tetrahedron Lett.*, 655 (1969).

(17) H. M. Frey, *J. Chem. Soc.*, 2293 (1962).

(18) Isobutyl carbene: T. Migita, C. S. Redvanly, and A. P. Wolf, presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968; butyl carbene: J. Figuera and A. P. Wolf, unpublished results.

(19) R. L. Russell and F. S. Rowland, *J. Amer. Chem. Soc.*, 90, 1671 (1968).

(20) Methyne has been shown to react with methane with a rate constant of 1.5×10^9 l. mol^{-1} sec^{-1}: W. Braun, J. R. McNesby, and A. M. Bass, *J. Chem. Phys.*, 46, 2071 (1967).

(21) M. J. Welch and A. P. Wolf, *Chem. Commun.*, 117 (1968).

(22) $\neq$ denotes a carbon atom with excess kinetic energy, of unspecified spin state while $[C^{11}RH]^*$ denotes the collision complex which has unspecified structure.

(23) This sequence does not imply that hot products are necessarily formed in one step from the carbene intermediate. It must also be noted that the excitation state of the carbene formed in reactions 3 and 5 are not necessarily the same.

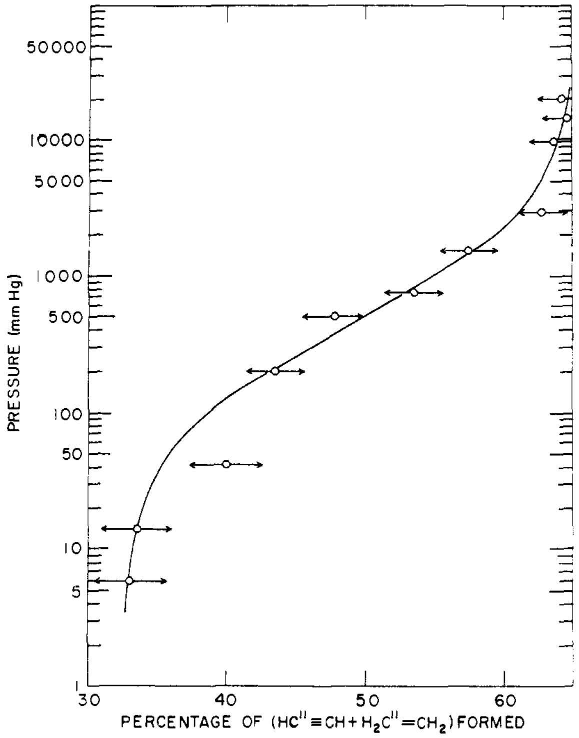

Figure 9. Methane, plot derived from eq 12: solid line, calculated values.

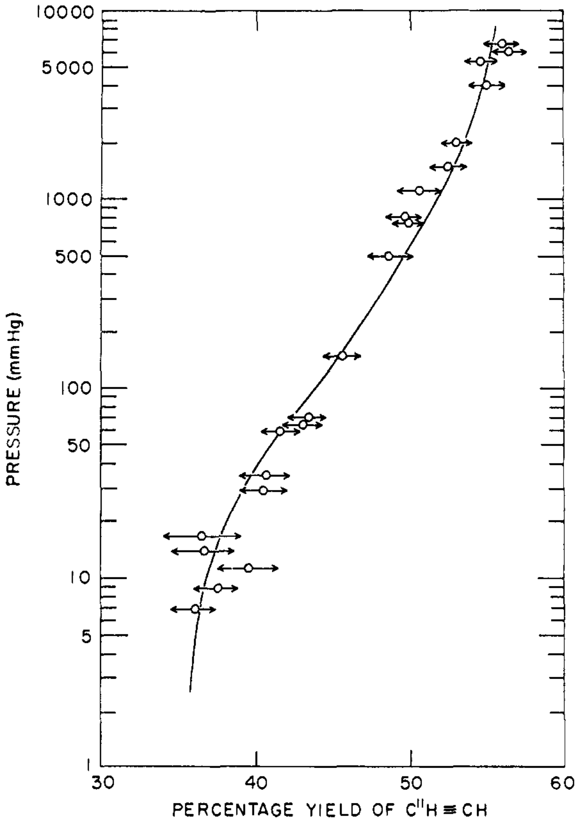

Figure 10. Cyclopropane, plot derived from eq 12: solid line, calculated values.

number of carbon atoms formed is very small relative to the number of substrate molecules, [RH] can be regarded as constant in a specific irradiation. Therefore since $\int_0^T(\mathrm{d}[\mathrm{C}^{11}]/\mathrm{d}t)\mathrm{d}t$ is the total $[\mathrm{C}^{11}]$ in the system which is proportional to the proton flux and since $\mathrm{d}[\mathrm{C}^{11}]/\mathrm{d}t$ is constant, then $\mathrm{d}[\mathrm{HP}]/\mathrm{d}t$ is also constant. The precentage hot yield is given by $100 \times (\mathrm{d}[\mathrm{HP}]/\mathrm{d}t)/(\mathrm{d}[\mathrm{C}^{11}]/\mathrm{d}t)$, and therefore the % hot yield can be expressed as

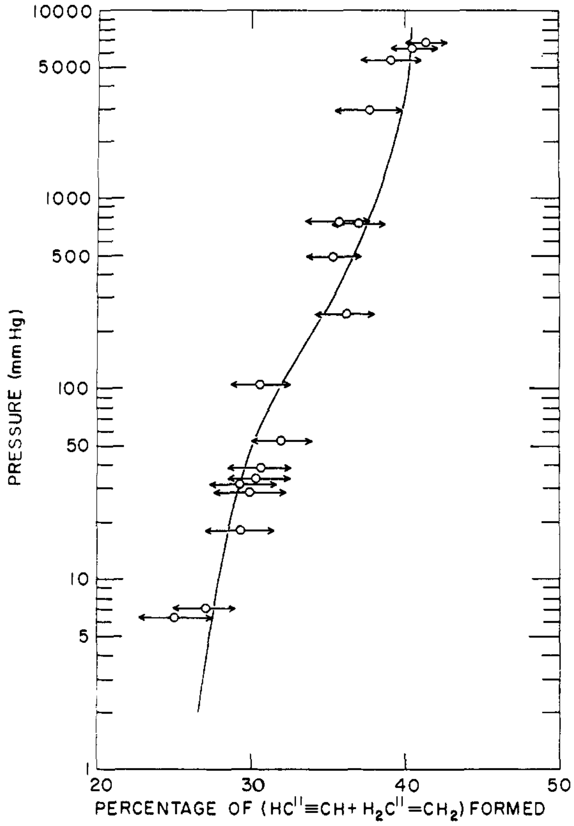

Figure 11. Propane, plot derived from eq 12: solid line, calculated values.

$$\%\ \text{hot yield} = \frac{100p(k_2 + k_4[\mathrm{RH}])}{(k_2 + k_3) + k_4[\mathrm{RH}]} \qquad (11)$$

Evaluation of these rate constants can be accomplished by making the further assumption that $[\mathrm{C}^{11}\mathrm{RH}]^*$ will have approximately the same collision frequency with RH as does RH with itself in the system studied.[24] Thus k_4 (l. mol^{-1} sec^{-1}) can be equated to the bimolecular collision frequency:[25] $k_4(\text{methane}) = 2.67 \times 10^{11}$, $k_4(\text{cyclopropane}) = 1.76 \times 10^{11}$, $k_4(\text{propane}) = 1.75 \times 10^{11}$, and $k_4(\text{neopentane}) = 1.41 \times 10^{11}$. Using these values of k_4 it is possible to try to fit a plot of eq 11 to the experimentally found results.

In the four cases studied, acetylene and ethylene (acetylene only in the cyclopropane case) are the only major hydrocarbon products, and the only hydrocarbon products in which pressure effects could be detected.[26] As a

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[24] The actual values of k_4 will be somewhat larger than those estimated due to the increased size of $[\mathrm{C}^{11}\mathrm{RH}]^*$ and the possible increase in kinetic energy of $[\mathrm{C}^{11}\mathrm{RH}]^*$ as compared to RH.

[25] These values have been estimated from molecular diameters (Å) $\sigma(\mathrm{CH_4}) = 3.800$, $\sigma(\mathrm{C_3H_6}) = 5.00$, $\sigma(\mathrm{C_3H_8}) = 5.06$, $\sigma(\mathrm{C_5H_{12}}) = 5.28$ (from J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley & Sons, Inc., New York, N. Y., 1964, p 1110) and average velocities (cm/sec) of the molecules, $\bar{c}(\mathrm{CH_4}) = 6.53 \times 10^4$, $\bar{c}(\mathrm{C_3H_6}) = 2.49 \times 10^4$, $\bar{c}(\mathrm{C_3H_8}) = 2.38 \times 10^4$, and $\bar{c}(\mathrm{C_5H_{12}}) = 1.46 \times 10^4$ (from G. W. C. Kaye and T. H. Laby, "Physical and Chemical Constants," Longmans Press, London, 1959).

[26] Products such as butadiene from cyclopropane or propene from propane occur in low yields (2–6% range). The errors in assay made the determination of pressure effects impossible.

Table I. Fitted Parameters for Eq 2

Hydrocarbon	100 p	k_2, sec^{-1}	k_3, sec^{-1}	k_2/k_3	$1/k_3$, sec
Methane	65.0	3.20×10^9	3.16×10^9	1.01	3.16×10^{-10}
Cyclopropane	55.7	9.72×10^8	5.35×10^8	1.82	1.87×10^{-9}
Propane	40.5	1.02×10^9	5.45×10^8	1.88	1.84×10^{-9}
Neopentane	53.5	1.19×10^9	3.40×10^8	3.52	2.96×10^{-9}

working hypothesis one can assume that the hot product yield is equal to the sum of the acetylene and ethylene yields. Thus, theoretical curves derived from eq 11 can be fitted to the experimental points by varying p, k_2, and k_3 to obtain minimum deviation. These curves are shown in Figures 9–12.

The best parameters for p, k_2, and k_3 are given in Table I, and Figures 9–12 show the curves[27] corresponding to these parameters. In addition the ratio k_2/k_3 is listed as is the value $1/k_3$.

It should be noted that if all carbon atoms form collision complexes as defined by [$C^{11}RH$]*, 100 × p should equal 100. Several effects can militate against the theoretical value and be responsible for the lower "best-fit" values given in Table I. We assume that acetylene and ethylene are the only hot products. This is, of course, an approximation. In addition some hot reaction between C^{11} and O_2 occurs at 4.5% added O_2, and this will also tend to reduce p.

The ratio k_2/k_3 is the ratio of collision complexes that do not need stabilization in order to react to those that produce thermalized carbon atoms unless collisionally stabilized. It appears that the smaller the hydrocarbon, the greater the percentage of collision complexes that need stabilizing. This is to be expected, because the smaller number of atoms in the molecule (actually the lower the number of degrees of freedom in the hydrocarbon), the lower is the energy that can be absorbed in the complex hence the greater the tendency to fragment.

The value $1/k_3$ gives a measure of the lifetime of the excited complex that fragments to thermalized carbon. Again, the more degrees of freedom in the hydrocarbon, the more energy the complex can absorb, and therefore, the larger the lifetime. This is, in fact, what is observed. It can also be seen that the yield of carbon monoxide-C^{11} shows a decrease at higher pressures which is smaller than would be expected from the increase in hydrocarbon yield. This effect can have several causes relating on the one hand to the changing reactive intermediate spectrum as the pressure is increased relative to reaction with oxygen (*e.g.*, [CH]* + O_2, [CH_2]* + O_2, etc.) and on the other hand to changing carbene reactivity with the substrate affecting the acetylene and ethylene yields in a different direction. The reactions of carbon atoms with oxygen will be the subject of a more detailed paper to be published later.[2b]

Conclusion

Evidence is presented to support the formation of a collision complex in recoil carbon atom reactions. The formation of some hydrocarbons are assumed to derive from a carbene intermediate which is formed by insertion of a carbon atom into a carbon hydrogen bond. Such a carbene would be vibrationally excited and would be expected to show the usual yield–pressure dependences in its fragmentation processes. The fact that the yield of fragmentation products such as acetylene goes up with increasing pressure must mean that there is a prior step which is pressure dependent. The hypothesis developed suggests that a collision complex is formed which then can go to form the carbene which is structurally and energetically capable of fragmenting to compounds such as acetylene. This complex may do so directly or *via* a stabilizing collision with the substrate. The model proposed is not inconsistent with phase-dependence studies.[2c,5,6] In a condensed phase, the carbene once formed is subjected to "immediate" stabilization and thus fragmentation processes are hindered. The ratios k_2/k_4 and k_2/k_3 may also be differently affected in the solid phase.

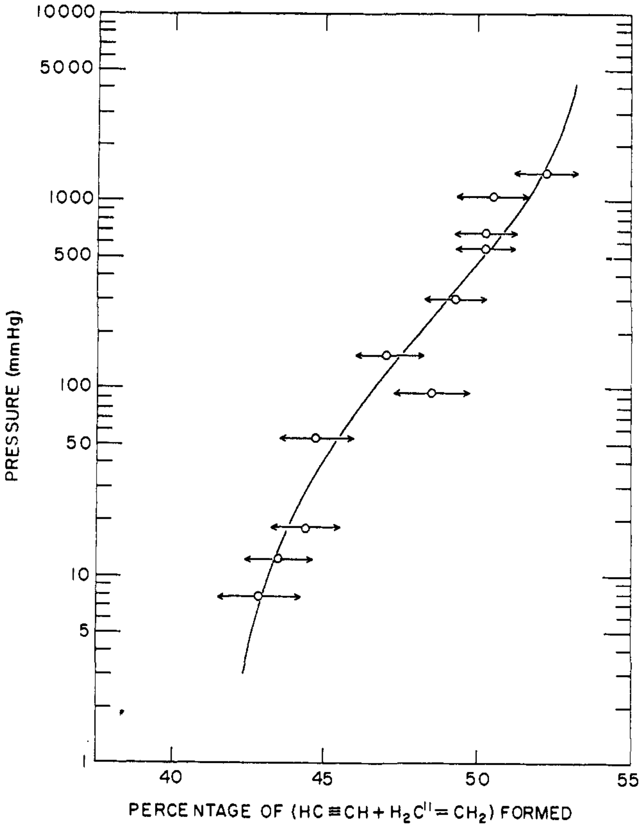

Figure 12. Neopentane, plot derived from eq 12: solid line, calculated values.

An interesting question arising from this work but not answered by it is how carbene-like the complex denoted by [$C^{11}RH$]* actually is? The complex [$C^{11}RH$]*

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[27] The curve fits the methane case better than a straight line (*cf.* Figure 2), and in the other cases the curves fit the summed data at least as well as they fit the straight line. It must, of course, be noted that the straight lines drawn in Figures 1–5 are merely the best straight lines one can draw through these points. It is perhaps not surprising that methane should give the best fit since the Σ of CO + C_2H_2 + C_2H_4 yield is closest to 100% of the products and therefore the Σ of C_2H_2 + C_2H_4 would be the best approximation to Σ of the hot products.

may be completely dissimilar to the carbene or it may be that $[C^{11}RH]^*$ is in fact a highly energetic but structurally distorted carbene requiring appreciable atomic motion to allow it to assume a well-defined singlet or triplet carbene structure. Further work is in progress in order to further elucidate this model.

The Rate of Thermal Decomposition of CF_3CN[1,2]

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Abstract In the temperature range above 684° the thermally initiated decomposition of CF_3CN yields C_2F_6 and $(CN)_2$, *i.e.*, $2CF_3CN \rightarrow C_2F_6 + (CN)_2$ (1). The reaction was shown to be second order in CF_3CN following the stoichiometry of eq 1 above. The rate of the decomposition was studied in the temperature range 684–809° with the resulting Arrhenius expression being $k_2 = 10^{11.7} \exp(-64.7 \pm 3.0\ k\text{cal}/RT)$ l./(mol sec).

The thermal stability of trifluoroacetonitrile was first reported by Janz and Stratta[3] in the temperature range 350–550°. Reactions of CF_3CN with mono- and diolefins have also been reported by Janz, *et al.*, in the same temperature range. The ethylene reaction results in the 1:1 adduct, *i.e.*, 4,4,4-trifluorobutyronitrile,[4] while the respective pyridines are formed with conjugated diolefins.[5] Since CF_3CN has only been studied relative to addition reactions, the thermal decomposition was undertaken in the temperature range 684–809°. The present communication reports the results of kinetic measurements for the reaction

$$2CF_3CN \longrightarrow C_2F_6 + (CN)_2 \qquad (1)$$

Experimental Section

Kinetic measurements were carried out in a 0.25-l. Vycor stirred-flow reactor with an on-stream sampling system described in detail elsewhere.[6] The rate of decomposition was studied in the temperature range 684–809 ± 2° using contact times between 464 and 2519 sec. Under these conditions, C_2F_6 and $(CN)_2$ were the only products observed. At temperatures above 809°, N_2 and other uncharacterized products were detected. The reaction mixtures were quantitatively analyzed on an Aerograph 204B gas chromatograph, equipped with hydrogen flame detectors, previously calibrated with pure samples of CF_3CN, C_2F_6, and $(CN)_2$.

The materials CF_3CN and C_2F_6 (Peninsular Chemresearch, Inc., 99% minimum) and $(CN)_2$ (Columbia Organic Chemicals Co., Inc., 99% minimum) were degassed under high vacuum and triply distilled at low temperatures prior to use.

Data and Results

The rate of thermal decomposition of CF_3CN was studied in the previously mentioned temperature range, using constant flow velocities (*i.e.*, contact times) through the reaction zone. The rate of decomposition was not affected by preconditioning the reactor surface (*i.e.*, CF_3CN pyrolyzed at ~800° using very long contact times).

The reaction order was determined by assuming both first- and second-order decomposition. The rate derivations are as follows.

A. If CF_3CN decomposes by a Lindeman type mechanism, the result is

$$CF_3CN \xrightarrow{k_1} CF_3\cdot + CN\cdot \qquad (2)$$

$$2CF_3\cdot \xrightarrow{k_2} C_2F_6 \qquad (3)$$

$$2CN\cdot \xrightarrow{k_3} (CN)_2 \qquad (4)$$

$$CF_3\cdot + CN\cdot \xrightarrow{k_4} CF_3CN \qquad (5)$$

Assumption of the stationary state for $CF_3\cdot$ in the reaction zone permits

$$0 = V_r k_1[CF_3CN] - V_r k_2[CF_3\cdot]^2 - V_r k_4[CF_3\cdot][CN\cdot] \qquad (6)$$

and

$$U_T[C_2F_6] = V_r k_2[CF_3\cdot]^2 \qquad (7)$$

where U_T is the total volumetric flow rate of the reactor effluent, *i.e.*, $U_{CF_3CN} + U_{C_2F_6} + U_{(CN)_2}$, and V_r is the volume of the reaction zone. If the assumption is made that $[CF_3\cdot] \simeq [CN\cdot]$, and $k_2 \simeq {}^1/_2k_4$, then

$$k_1 = \frac{3U_T[C_2F_6]}{V_r[CF_3CN]} \qquad (8)$$

which, upon rearranging gives

$$\frac{U_T}{V_r} = k_1\frac{[CF_3CN]}{3[C_2F_6]} \qquad (9)$$

A plot of U/V *vs.* $[CF_3CN]/[C_2F_5]$ should result in a straight line with a slope of ${}^1/_3k_1$ if the order and mechanism are correct.[7] Figure 1 depicts such a curve. It appears that the plot is not a "good" straight line; thus, first-order kinetics are assumed to be invalid.

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[1] Based in part on a thesis submitted by D. J. P. in partial fulfillment of the requirements of the Ph.D. degree, Rensselaer Polytechnic Institute, June 1968.

[2] Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

[3] G. J. Janz and J. J. Stratta, *J. Org. Chem.*, **26**, 2169 (1961).

[4] J. B. Flannery and G. J. Janz, *J. Amer. Chem. Soc.*, **88**, 5097 (1966).

[5] G. J. Janz and A. R. Monahan, *J. Org. Chem.*, **29**, 569 (1964); and A. R. Monahan and G. J. Janz, *J. Phys. Chem.*, **69**, 1070 (1965).

[6] D. J. Perettie, R. J. Tofte, and G. J. Janz, *Chem. Instr.*, **1**, 221 (1968).

[7] W. C. Herndon, *J. Chem. Educ.*, **41**, 42 (1964).