Polymer Production in the γ Radiolysis of Methane in Liquid Argon[1]

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Abstract: γ radiolysis of methane produces a polymer which in the condensed phase has an average molecular formula $C_{20}H_{40}$. An attempt to study the mechanism was made by using the ionization caused by electron transfer from methane to argon ions in liquid argon. The γ radiolysis of liquid argon–methane solutions showed that in mixtures containing as little as 0.15 mole % methane, a polymer averaging $C_{22}H_{42}$ was produced with a G value 11 times that for the polymer from pure methane. This G value is calculated on total energy absorbed by the sample. It is suggested that the polymer is formed by condensation of the dense blob of methane fragments which could be formed by Auger electrons emitted following inner-shell ionization. This ionization would be highly localized.

The γ radiolysis of solid methane at 77°K yields a highly branched polymer [$G(-CH_4$ to polymer$) = 0.3$] with a dose-independent average formula of $C_{20}H_{40}$.[2] Information available about the polymer produced places several restrictions on possible mechanisms of formation. Nmr data show the average molecule has eight methyl groups with the rest being CH_2 and CH groups. Heat of combustion data indicate that the polymer formation is about 9 eV/molecule endothermic. The most interesting observation was that the average size of polymer was shown to be dose independent up to 150 Mrads. No mechanism of polymer growth involving secondary reactions of product molecules with the primary methane ions can yield a material of dose-independent size. Even if some kind of steady-state polymer growth and shrinkage were somehow achieved, there would be an initiation dose required below which polymer seeds would not have reached full size. Since the normal polymer yields and size are achieved at the lowest dose examined (4 Mrads), an initiation dose is ruled out.

Since there is very efficient energy transfer to hydrocarbon dissolved in a liquid rare gas,[3-5] we have irradiated solutions of methane in liquid argon to look for effects of concentration on polymer formation. In such solutions these certainly would be very efficient energy transfer to methane, and dilution of the methane by argon ought to drastically reduce yields from the single initiation but not from a one-step single event process. An attempt has been made to understand more about the polymer formation.

Experimental Section

Samples were irradiated with Co^{60} γ rays (mainly at dose rates near 0.3 Mrad/hr) in full 250-ml Pyrex ampoules under liquid nitrogen or argon. Filling of samples and purification of methane is as described earlier.[2] Methane was added by measured liquid volume, accurate to 10% or so. Matheson ultrahigh purity argon was added to the methane in the ampoules without further purification and determined by weighing the total sample. Radiolysis of a pure argon sample gave no polymer, and no oxygen was found in the polymers produced.

After radiolysis, the samples were broken open under "hi-pure" nitrogen and the volatiles were allowed to evaporate. The cells containing polymer then were flushed with about 20 l. of nitrogen in 10 min and weighed. Polymer samples for vapor-pressure osmometer molecular weights, CH analysis, and nmr and chemical ionization mass spectra were removed by eyedropper, as was the petroleum ether (bp 35°) used to wash out residual polymer. The cells then were reflushed and reweighed to get polymer G values, which are accurate to 10% or better.

Average molecular weights (using benzene solutions) and nmr analyses were done as described previously.[2] Chemical ionization mass spectra were done by Dr. F. H. Field, Esso Research and Engineering Co., Linden, N. J.[6]

All G values were calculated using the total energy absorbed by the sample, corrected for electron/gram differences between the Fricke dosimeter, argon, and methane. The cells used are thick enough so that differences in stopping power of the samples affect the dose rates relative to the water dosimeter. Calculations show this effect changes the dose rate to liquid Ar by a factor of 0.99 and methane dose rates by 1.09 relative to water.

Results

Experimental results are shown in Table I. The polymer nmr looks just like that found with pure methane as shown in a previous paper.[2] Drawing arbitrary divisions for $C_{22}H_{42}$ one gets 55% methyl protons and 45% CH_2 and CH protons (divided about 3 to 2). This distribution means about eight methyl, six CH_2, and eight CH carbons. Preliminary analysis of the chemical ionization mass spectra shows alkanes, single-ring naphthenes, and double-ring naphthenes in a ratio of roughly 1:3:5. There is insufficient information on fragmentation of such large branched molecules to determine the molecular weight spread, but the spectra are not inconsistent with the osmometer average molecular weights.

The average formula of the polymer made in the most dilute solution of methane (0.15 mole %) is $C_{22}H_{42}$, and the size does not change much as the methane concentration is increased to 15 mole %. A gradual increase in size then ensues with further methane enrichment. The average formula $C_{28}H_{54}$ results from a 50 mole % methane run, and a 78 mole % methane polymer came out $C_{36}H_{70}$. Hydrocarbons larger than

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Table I. Data on Polymer from Methane–Argon Solutions

Dose, Mrads	Mole % CH_4	G ($-CH_4$ to polymer)	Av mol wt	Av formula^c	Nmr protons % CH_3	Nmr protons % $CH + CH_2$
14^a	0.15^d		304	$C_{22}H_{42}$	53	47
11^a	0.15	1.3	310	$C_{22}H_{42}$		
16^a	0.63^d	...	316	$C_{22}H_{42}$	55	45
11^a	1.4	1.3	309	$C_{22}H_{42}$		
8.5^a	3.2	1.3	306	$C_{22}H_{42}$	56	44
10^a	4.9	1.3	311	$C_{22}H_{42}$		
11^a	11.0	1.4	315	$C_{22}H_{42}$		
39	16	1.2	309	$C_{22}H_{42}$	59	41
9	15	1.0	304	$C_{22}H_{42}$		
21	20	1.1	314	$C_{22}H_{42}$	55	45
10	20	1.0	364	$C_{26}H_{50}$		
10	29	0.95	381	$C_{27}H_{52}$		
20.5	30	0.94	351	$C_{25}H_{48}$	59	41
38	31	0.96	321	$C_{23}H_{44}$	60	40
39	36	0.66	348	$C_{25}H_{48}$	61	39
9	37	0.65	394	$C_{28}H_{54}$		
10.5	39	0.68	391	$C_{28}H_{54}$		
21.5	42	0.55	378	$C_{27}H_{52}$		
21.5	50	0.50	387	$C_{28}H_{54}$	63	37
33	46	0.58	369	$C_{26}H_{50}$		
17^a	68	0.32	513^b	$C_{37}H_{72}$		
18^a	78	0.20	503^b	$C_{36}H_{70}$		

[a] Irradiated under liquid argon (87°K); others irradiated at 77°K.
[b] May be too high if polymer is not completely soluble in benzene.
[c] To nearest whole C, based on molecular weight and C, H analysis.
[d] Irradiated at 0.6 Mrad/hr.

about C_4 are not soluble in liquid argon, so the polymer precipitates and floats to the top of the dense liquid.

Discussion

The $G(-CH_4$ to polymer) values increase from $G = 0.20$ in 78 mole % methane to $G = 1.3$ in 0.15 mole % methane. In terms of polymer molecules (which are larger at high methane concentration), there is an 11-fold increase in yield going from high CH_4 to high Ar concentration. Since these values are based on the total energy absorbed by the mixture, complete energy transfer from argon to methane would result in no change in G, everything else being equal.

The data pose the question: How can a heavy hydrocarbon be made in a primary event from 0.15 mole % CH_4 in argon with a G value 11 times that for 78 mole % CH_4? Indeed, in the dilute solutions almost as much methane is lost to polymer as goes to ethane, the only other major product. ($G(-CH_4$ to ethane) $\approx$ 2.0 at all concentrations.[5]) The ethane yield can be explained in terms of energy transfer to methane followed by reaction of individual ions or neutral fragments.[3,5] However, at such low concentrations the mechanism of polymer production in such yields is less obvious. Since the G values are based on the total energy absorbed by the solution, energy transfer alone cannot explain an *increase* in yield of polymer. A single initiator mechanism would have predicted a decline in polymer yields at low concentration. Furthermore, neutral methane fragments could not hold the 9 eV of energy required,[2] and ions might not have time to gather enough methane before electron recombination. The polymer must come from combination of a number of methane fragments produced in a small region or involve successive ionizations (or excitations) in disagreement with the observation that the molecular weight is dose independent in both solid methane[2] and in the argon solutions (Table I). The nmr data require that about equal quantities of CH_3, CH_2, and CH be involved.

Whereas obtaining and holding the required energy is the main problem with single initiators, a high density of reactive fragments would have no such troubles. The problem with this mechanism is how such a high-energy density of the energy delivered by Co^{60} γ rays is finally placed in the absorber (water, in the case considered) by electrons between 100 and 500 eV in energy. Such electrons are scattered as they ionize and excite molecules in the medium in a short random walk which yields a small, roughly spherical region of ionization and excitation called a "blob." Polymer could be made in this blob, but, since these straight scattering calculations are not medium dependent, this approach would predict the same yield of blobs in methane and argon.

We suggest another possible mechanism of producing such a high local concentration of fragments. This could be Auger electron emission following inner-shell ionization. A 206-eV Auger electron and an Ar^{2+} are the major products from ionization of the 245–247 eV L levels of argon.[7] K ionization of argon requires 3200 eV and yields a variety of Auger electrons and positive ions up to Ar^{+}.[7,8] Carbon K ionization gives a 246-eV Auger.[9] The low-energy electrons thus made will be scattered in a short, random-walk path and will produce a small sphere containing a number of ions and excited neutrals. Since the local concentration of these fragments would be very high, they could combine with one another to produce a large molecule before diffusion separated them. (Since no decrease in polymer size is seen at 0.15 mole % CH_4, the sphere must be at least large enough to contain 20 methanes, *i.e.*, about 100 Å in diameter.) In the low methane concentration runs, the initial species produced would be made from argon by argon Augers, but rapid charge and excitation transfer reactions to methane will occur just as they do for isolated species. (Methane has a lower ionization potential.) Electron recombination with likely methane ions such as CH_4^+ and CH_3^+[10] could give $CH_2 + H_2$ and $CH + H_2$. Excitation transfer to CH_4 is known to give $CH_3 + H$ and $CH_2 + H_2$.[11] H atoms might interfere with condensation of fragments to polymer, but molecular H_2 could not. At high methane concentrations, carbon K Augers would be operating directly on methane, and this different excitation process plus the greater availability of methane would account for the increased size of the polymer produced.

Since we suggest that the polymer might result from inner-shell ionization and ethane primarily from valence ionization, a look at the partition of energy between these two possibilities in CH_4 and Ar can test our hypothesis. Experimental measurements for argon[8] show that L ionization has a cross section of about 5% of that for valence electron removal. K ionization was found to be relatively insignificant. These relative

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cross sections were shown to be independent of energy above a few hundred electron volts up to 15 keV and should remain so over the range of electrons produced by Co^{60} γ rays. The argon L electron has about a 250-eV ionization potential as opposed to about 16 eV for the valence electron, so L ionization receives about 45% of the total energy absorbed by argon. In high argon mixtures, 40% of the methane converted goes to polymer; *i.e.*, $G(-CH_4$ to polymer$)/[G(-CH_4$ to polymer$) + G(-CH_4$ to ethane$)] = 1.3/(1.3 + 2.0) = 0.40$. Thus our hypothesis does predict the experimental results.

In the case of methane, the lower relative cross section for carbon K ionization means this process receives approximately an estimated 4% of the energy absorbed.[12] In pure condensed methane $G(-CH_4$ to ethane$) = 4.6$,[2,13] intermediate size products have $G(-CH_4) = 0.3$,[2] and polymer is $G(-CH_4) = 0.2$–0.3 (liquid and solid phase). Thus polymer accounts for about 5% of the G for methane lost in condensed-phase methane, a number which again correlates well with the energy going into inner shell ionization.

Another way of stating these correlations is that the ratio of energy going to argon L *vs.* carbon K ionization is about 11(45/4), which is the same as the ratio of G's for polymer made in high argon *vs.* high methane radiolysis.

In hot-atom chemistry Auger processes have been known to be important for a long time. The chemical consequences of nuclear isomeric transitions and internal conversion of γ rays have come to understanding in this way.[14,15] The search for inner-shell ionization effects is an old one, too, with some evidence of success,[12,15] but the present evidence emphasizes the possible differences between the effects of inner- and outer-shell ionization in radiation chemistry.

Of course as suggested earlier[2] the hydrogen-deficient positive ions which are rich in energy, CH_n^+ ($n = 0, 1, 2, 3$), may be the source of the polymer, and we must remember that 584-Å light (21-eV energy) which is of too low energy to make Auger electrons also gave polymer,[16] although in this case the polymer was less well characterized. Recently Olah and Schlosberg[17] have reported that the chain polymerization can run downhill energetically once CH_3^+ is initially formed. The variation in polymer yield with the energy-absorbing material might be explained by an increase in the production of species such as CH_3^+ when methane is ionized by charge transfer from argon ions.[18] However, in the dilute liquid solutions the predominant Ar_2^+ ion[4] (recombination energy about 13.7 eV)[19] cannot deliver enough excitation energy to methane to produce many fragment ions like CH_3^+.

In conclusion, the production of polymer in the dilute argon solutions gives another set of limiting conditions on the mechanism of polymerization of methane by ionizing radiation, and furthur experiments are under way.

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Spectroscopic Studies on the α-Phenylated Naphthalenes[1]

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Abstract: The fluorescence and phosphorescence emission spectra of the six α-phenylnaphthalenes are described. On increased phenyl substitution bathochromic shifts are observed for both transitions, the phosphorescence lifetimes decrease, and the ratio of phosphorescence to fluorescence diminishes. The energy available from triplet–triplet annihilation is reduced more rapidly than the energy of the lowest singlet state as successive phenyls are added to naphthalene. If an analogous relationship exists for tetracene and the phenylated tetracenes, then T–T annihilation in rubrene (5,6,11,12-tetraphenyltetracene) will fail to generate the fluorescent singlet state because of an energy insufficiency of ~5 kcal/mole. The significance of these results to the mechanism of electron-transfer luminescence is discussed. The properties of all of the α-phenylnaphthalenes, including their nmr spectra, are best accounted for by pπ–pπ overlap of nonperpendicular adjacent orbitals rather than by spiroconjugative interaction.

Polycyclic aromatic compounds are often both fluorescent and phosphorescent. These characteristic properties are invaluable tools for elucidating other photophysical and photochemical behavior. When such molecules are multiply substituted by phenyl groups to form compounds such as rubrene (5,6,11,12-tetraphenyltetracene) and 9,10-diphenylanthracene, the products exhibit strong fluorescence, but no phosphorescence is observed. The usually intense fluorescence of such compounds has been explored and utilized, but the

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