that controls the radiative lifetimes of these complexes also plays a dominant role in determining the quenching rate constants. This mechanism corresponds to an indirect coupling of the luminescing and ground states through a higher energy charge-transfer state.

Our previous suggestion that a large $(d\pi^*) \rightarrow (\pi\pi^*)$ configuration interaction occurs in $[IrCl_2(diphenylphen)_2]Cl$[12] is further supported by the results of the present study. The long radiative lifetime and small value of $K|M_{SO}|^2$ obtained for this complex indicate that its luminescence, in contrast to the others (see Figure 4), does not originate from a simple charge-transfer transition. The lowest excited state of this complex appears to be classified best as a level localized primarily on the ligands that is highly perturbed by the close proximity of a charge-transfer excited state.

For all but one of the iridium species studied here our observations indicate that a "delocalized molecular" description of the emitting states, as suggested by DeArmond and Hillis,[13] is not necessary. Our data show that, aside from $[IrCl_2(diphenylphen)_2]Cl$, the $K|M_{SO}|^2$ values are large, indicating a strong admixture of singlet character in the emitting triplet level, a characteristic that we associate with a charge-transfer level. Although ligand-localized triplet states are certainly closer to the emitting levels in iridium complexes than they are in ruthenium ones,[13] the classification of an excited state as "delocalized molecular" should be necessary only when the energy gap between the zero-order $d\pi^*$ and $\pi\pi^*$ triplet states is comparable to the interaction matrix element. Only for $[IrCl_2(diphenyl)_2]Cl$ do we infer that this condition obtains. Studies of several other iridium(III) molecules indicate that the matrix element mixing charge-transfer and ligand-localized triplet states is only on the order of several hundred wavenumbers.[34] Since the energy gaps between the unperturbed ligand triplets and the emitting levels are several times larger than this value for the unsubstituted iridium(III) species, we conclude that small $(d\pi^*) \rightarrow (\pi\pi^*)$ interactions occur and that the appellation "charge transfer" is an adequate description of the emitting levels.

The most striking effect of phenyl substitution of these nitrogen-coordinated ligands is the large increase produced in the luminescence yields of the respective chelates. Thus phenyl substitution can be used to "fine tune" the optical properties of a complex, in this instance, to improve the efficiency of the luminescence, without, in most cases, changing the fundamental nature of the transition responsible for it.[12] High efficiency is of paramount importance in the design of quantum converters and laser materials.

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[34] R. J. Watts and G. A. Crosby, Abstracts, 26th Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, June 1971, No. W6.

Polymer Production in the γ Radiolysis of Methane, Ethane, and Ethylene Solutions in Liquid Argon

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Abstract: Further studies of the products of radiolysis of solutions of methane, ethane, and ethylene in liquid argon have been made. Our earlier work left the question of mechanism somewhat unanswered. The additional data seem to show that the most probable mechanism is ionization of the solutes with lowest ionization potential (IP) by electron transfer to the argon ions initially produced by the γ rays and subsequent ion molecule reactions and neutralization to form the heavy hydrocarbons. The limit on molecular weight is suggested to be an energetic one in which further growth of the polymer ion is energetically forbidden. Charge-transfer recharges the polymer when it is neutralized and this is thought to happen several times.

The reactions of hydrocarbons under the influence of ionizing radiation have been studied extensively for many years. One of the most interesting products found from methane, ethane, and ethylene under various conditions is an oily material referred to as a polymer as a matter of convenience. This polymer has been observed from gas discharge reactions,[1] methane photolysis,[2] and the radiolysis of methane under various conditions.[1c,3,4]

γ-Radiolysis of solid methane at 77°K produces a polymer with an average molecular formula $C_{20}H_{20}$.[4d-f] The yield is proportional to dose (constant G value) and the molecular weight is independent of dose as well. It was proposed that the reaction occurred *via* a chain

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[1] (a) A. K. Brewer and P. D. Kueck, *J. Phys. Chem.*, **35**, 1293 (1931); (b) L. M. Yeddanapalli, *J. Chem. Phys.*, **10**, 249 (1942); (c) L. W. Seick and R. H. Johnsen, *J. Phys. Chem.*, 67, 2281 (1963).

[2] (a) D. C. Waker and R. A. Back, *J. Chem. Phys.*, **38**, 1526 (1963); (b) E. M. Magee, *ibid.*, **39**, 855 (1963); (c) C. A. Jensen and W. F. Libby, *ibid.*, **49**, 2831 (1968).

[3] P. Hamlet, J. Moss, J. P. Mittal, and W. F. Libby, *J. Amer. Chem. Soc.*, **91**, 258 (1969).

[4] (a) S. C. Lind and D. C. Bardwell, *J. Amer. Chem. Soc.*, **48**, 2335 (1926); (b) R. W. Hummel, *Nature (London)*, **192**, 1178 (1961); (c) G. J. Mains and A. S. Newton, *J. Phys. Chem.*, **65**, 212 (1961); (d) D. R. Davis and W. F. Libby, *Science*, **144**, 991 (1964); (e) P. Ausloos, R. E. Rebbert, and S. G. Lias, *J. Chem. Phys.*, **42**, 540 (1965); (f) D. R. Davis, W. F. Libby, and W. G. Meinschein, *ibid.*, **45**, 4481 (1966); (g) L. Kevan and W. F. Libby, *ibid.*, **37**, 2496 (1962); (h) *ibid.*, **39**, 1288 (1963); (i) D. R. Davis, W. F. Libby, and L. Kevan, *J. Amer. Chem. Soc.*, **87**, 2766 (1965).

Table I. Solid Methane at 77°K

	Dose rate, Mrad/hr	Dose, Mrad	Amount irradiated, g	*G* values						
				H_2	Ethane	Ethylene	Propane	Propylene	Butane	Pentane
UCLA[4d,f]	0.07–0.7	8–100	20–100		2.1		0.07		0.11	0.44
					2.1		0.002		0.0024	0.0016
NBS[4e]	9.0	0.6–6.0	0.7–1.4	2.87	2.30	<0.0003	0.052	<0.0005	0.038	0.020

reaction. Chain initiation was believed to be accomplished by highly reactive, hydrogen deficient ions from methane, such as CH_2^+, CH^+, or C^+. A similar mechanism was proposed earlier by Hummel for the gas phase reaction.[4b] Our current position is very similar.

There appear to be, at first glance, some inconsistencies in the literature in that some workers do not deal with the polymer while others find it to be one of the main products. Following on the early work of Lind and Bardwell (1926),[4a] Brewer and Kueck (1931),[1a] Yeddanapalli (1942),[1b] Hummel (1961),[4b] Mains and Newton (1961),[4c] and Sieck and Johnsen (1963),[1c] all of whom reported polymer to be produced to varying degrees of certainty, our UCLA group undertook to study pure solid methane at 77°K[4d,f] at about the same time as the National Bureau of Standards group.[4e] The work on methane followed earlier work on *n*-heptane at 77°K.[4g,h] A comparison of the results for the light hydrocarbons is made in Table I.

The NBS data did not include the polymer yield. The amount of sample used was only a few per cent of that used at UCLA and the total doses were about tenfold lower as well. However, for the light products there is acceptable agreement between the sets of data displayed in Table I.

The data of Ausloos, *et al.*,[4e] at the NBS included excitation by transfer of charge or excitation energy from argon in excess, 46.8:1 mole ratio, at 77°K. This presumably was a solid matrix or a glass and gave yields (calculated on total energy absorbed by the entire system) which were similar to those quoted in Table I for pure solid methane: 2.28 for hydrogen, 0.93 for ethane, 0.070 for propane, 0.042 for butanes, and 0.070 for the pentanes.

The technique of using noble element liquids for solvents to study excitation transfer to solute hydrocarbon in place of the solid matrices or solid solutions of the NBS group was used shortly afterward at UCLA in the *n*-hexane xenon system.[4i] This worked well and gave results essentially identical with those found in solid *n*-heptane at 77°K even though the temperature was much higher at 195°K (the irradiation cells were under some pressure).

The next work on the methane–argon system was done by Klassen[4,5] at 91°K at concentrations of methane ranging down to 0.05 mol % with results very similar to those given in Table I and fitting well the early matrices or glass results of Ausloos, *et al.*[4e] Thus it was now firmly established that excitation transfer is essentially complete down to concentrations less than 0.1 mol %. However, no evidence was given for polymer formation.

The next development was our work on polymer production from the solution of methane in liquid argon[3] showing it to be produced in about the same yields as had been found in the earlier work on pure solid methane. The molecular weights and chemical and physical properties were very similar, something like $C_{25}H_{50}$ with a highly branched saturated structure.

For ethylene solutions in liquid argon, Klassen[5] reported the light hydrocarbon yields for concentrations from pure ethylene to 0.046 mol %, the distribution changing relatively little The doses were low enough so only a small percentage of ethylene was consumed in most cases. Our results for the light hydrocarbons (Table VII) differ in several respects probably due to our much higher doses, 2.5 *vs.* 0.06 Mrad, but the most marked difference is the polymer which Klassen does not discuss. He does determine the total loss of ethylene at 0.43 mol % concentration to be about 15 molecules per 100 eV of energy absorbed (*G*) which considerably exceeds his reported yields of products in similar concentration ranges and he notes that this probably means higher molecular weight hydrocarbons are being produced.

For methane and ethane and their solutions in liquid argon, Klassen[6] reported results similar to those for ethylene. At the low doses used, light hydrocarbons were the products reported but a single measurement at 0.1 mol % ethylene in argon showed the loss of ethylene to considerably exceed the total of the yields of measured products and Klassen notes here again that this suggests some high molecular weight products were formed.

Present Research

In order to determine the mechanism for polymer production, a number of additional experiments on argon solutions have been carried out. These centered on the low methane concentration range and included ethane and ethylene as solutes as well. The results of these experiments, coupled with the wealth of information in the literature, hopefully have led us closer to the mechanism. An effort to attain an overall material balance has been made.

Experimental Section

Reagents and Apparatus. Methane used in the experiments was Matheson ultra high purity grade. Ethane and ethylene were Matheson CP grade. Purification was accomplished as described previously.[3] Matheson ultra high purity argon ($O_2 \leq 1$ part per million) was used as received.

The irradiation cells and Pyrex vacuum system were described previously.[3] The argon-hydrocarbon samples were prepared as reported previously.[3] All samples were irradiated in the 10-kCi ^{60}Co source of the Laboratory of Nuclear Medicine and Radiation Biology at UCLA. A dose rate of 0.25 Mrad/hr, as determined by the Fricke dosimeter, was used.

Analysis of Products. Samples in which only polymer was analyzed were handled as previously.[3] Samples in which all products except H_2 gas were examined were evaporated into a

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(5) N. V. Klassen, *J. Phys. Chem.*, 71, 2409 (1967).

(6) N. V. Klassen, *ibid.*, 72, 1076 (1968).

stream of "high-pure" nitrogen. The gas stream was periodically passed through a gas chromatograph with an 8-ft, $^{1}/_{4}$-in. column of Porapak R operating at room temperature. A flame-ionization detector was used. Analyses were made every 20 min throughout the 18–24 hr required for evaporation of the entire 50–250 cc of liquid argon solution. The total amount of hydrocarbon present was determined by integrating a plot of peak area *vs.* time of injection.

Following evaporation, the reaction cell was warmed to room temperature and the light hydrocarbons (C_3–C_{10}) were removed by distillation at room temperature into an evacuated cell cooled in liquid nitrogen. The distillate was then vaporized and injected with a gas tight syringe onto a 30-ft column of 20% B,B′-oxydipropionitrile on Chromosorb P. The relative yields of products were determined from the chromatogram and the absolute yields from the weight of light hydrocarbon removed.

Intermediate size hydrocarbons (C_{10}–C_{18}) were distilled in a similar way at a temperature of about 40°. The removal was considered complete when the sample could be flushed for 15 min with "high-pure" nitrogen at 40–80 l./hr with no loss in weight to the sample. The polymer was then analyzed as before.[3] The polymer could usually be observed floating as a film on the liquid argon solution.

Molecular weights of the polymer were determined with a Mechrolab vapor pressure osmometer, Model 301A. Benzene was used as a solvent and benzil as the calibration standard. Checks with eicosane showed accuracy to be within ±10%.

Carbon, hydrogen microanalysis was performed by Miss Heather King of the UCLA chemistry department. Nmr spectra were recorded on a Varian Associates A-60 instrument. Peak areas were measured both electronically and by triangulation. The polymer from ethane and methane were run in a CCl_4 solution. The ethylene polymer was run neat. Infrared spectra were run on a smear of the polymer on a sodium chloride window.

Samples of each type were evaporated without irradiation and no materials, other than starting materials, were present. The energy absorbed was measured for the entire sample by making the appropriate corrections for electron/gram fractions of the various components relative to water. Dose rates were measured with the Fricke dosimeter[3] in the same type of cells used for radiolysis.

A small sample of pure polymer was irradiated in a vacuum with a dose of 100 Mrad and analyzed for molecular weight and gaseous products formed.

Results

Results from the radiolysis of methane–argon solutions are given in Tables II and III. The mean value for *G*(polymer) is about 0.08 over a tenfold concentration change from 0.15 mol % to 1.5 mol %. The value is slightly higher than reported previously,[3] when the total dose corresponded to a methane conversion of about 300% if *G*(-CH_4) is 10. As Table II shows, *G*(polymer) is essentially constant in the range of methane conversion of 28–100%.

Table II. Methane–Argon Solutions (Polymer Only)

Mol % CH_4	Dose, Mrad	*G*(polymer)	Mol wt, g	Av formula
0.15	3.9	0.084	312	$C_{22}H_{44}$
0.15	3.9	0.11	297	$C_{21}H_{42}$
0.16	13.5	0.064	310	$C_{22}H_{44}$
0.59	13.5	0.057	311	$C_{22}H_{44}$
0.66	10	0.10	312	$C_{22}H_{44}$
1.5	10	0.08	314	$C_{22}H_{44}$
1.5	10.3	0.04	300	$C_{21}H_{42}$

Average formula of the polymers in Table II were assigned on the basis of best fit to C, H analysis and molecular weight. Nmr spectra of the polymer were similar to those reported previously.[3] The spectra were used to qualitatively determine molecular shape. A dividing line at δ 1.15 separated methyl from all other types of protons.[7] A second division at δ 1.58 was used to separate methylene from methine protons. Using this method the ratio of groups, CH_3:CH_2:CH, is about 4:3:4, indicating a high degree of branching.

Table III. Methane–Argon Solutions (Complete Analysis)

Product	0.15 mol % CH_4, *G*(product) (%)	0.076 mol % CH_4, *G*(product) (%)
Ethane	2.4 (61)	1.3 (1.2)
Propane	0.049 (1.8)	0.64 (18)
n-Butane	0.004 (0.2)	0.15 (5.5)
n-Pentane	0.002 (0.1)	0.082 (3.8)
n-Hexane	0.003 (0.2)	0.077 (4.2)
(C_3–C_{10}) Av $C_{3.3}$	0.062 (2.6)	Av $C_{3.2}$ 0.042 (1.2)
(C_{10}–C_{18}) Av C_{10}	0.16 (20)	0.64 (59)
Polymer ($C_{22}H_{44}$)	0.05 (14)	0.017 (3.4)
Dose (Mrad)	2.5	2.5
-CH_4	8 ± 0.5	11 ± 1

Table IV. Ethane–Argon Solutions (Polymer Only)

Mol % C_2H_6	Dose, Mrad	*G* (polymer)	Mol wt, g	Av formula
0.22	10.33	0.19	297	$C_{21}H_{42}$[a]
0.33	10.3	0.21	338	$C_{24}H_{50}$[b]
0.42	12.5	0.20	289	$C_{21}H_{42}$
0.45	10.3	0.21	346	$C_{25}H_{50}$[c]
0.51	1.0	0.20		
0.66	10.3	0.24	372	$C_{27}H_{54}$[d]

[a] n^{25}D 1.5419. [b] n^{25}D 1.5421; CH_3:CH_2:CH = 4:3:3. [c] n^{25}D 1.5419; CH_3:CH_2CH = 4:3:3. [d] n^{25}D 1.5418; CH_3:CH_2:CH = 4:3:3.

Infrared spectra of the polymer were like those obtained in solid methane radiolysis.[4f] They show a high concentration of methyl groups and few, if any, CH_2 straight chains longer than three carbon units.

The results in Table III are for samples in which all products were analyzed. Only straight chain paraffins were detected. All compounds not reported have $G < 10^{-4}$. The intermediate products (C_{10}–C_{18}) were analyzed by gas chromatography. They consisted of a large number of isomers, indicated by a large, poorly defined chromatogram covering retention times expected for the entire range of straight chain and some branched chain paraffins in that molecular weight range. The chromatogram showed a tendency toward decreasing yield with increasing molecular weight.

At a concentration of 0.076 mol % a dramatic shift in products was observed. A fourfold increase was observed in the yield of intermediate size hydrocarbons, while the average light hydrocarbon yield decreased slightly. The polymer yield fell sharply, and, even with the most stringent allowances for error, the yield is only one-third to one-fourth of that at 0.15 mol % methane. At the low concentration, the methane was nearly totally consumed so the drop in polymer yield is readily understood on the accretive mechanism proposed (*cf.* Discussion).

A small sample of the methane polymer was irradiated under vacuum with 100 Mrad. No measurable amounts of gaseous products were formed. The molecular weight of the polymer remained constant within experimental error.

The results for the radiolysis of ethane in liquid argon are given in Tables IV and V. The polymer from eth-

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(7) R. M. Silverstein and C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1963, p 82.

Table V. Ethane–Argon Solutions (Complete Analysis)

Product	*G*(product)
Methane	0.17
Propane	0.041
n-Butane	0.15
n-Pentane	0.005
n-Hexane	0.002
n-Octane	0.005
(C_3–C_{10}) Av $C_{3.9}$	0.20
(C_{10}–C_{18}) Av C_{10}	0.39
Polymer	0.13
Dose (Mrad)	2.5
Mol % C_2H_6	0.15
$G(-C_2H_6)$	3.85

ane was the same as that from methane, based on molecular weight, nmr, ir, and C, H analysis. The *G* for loss of ethane to polymer was 2.0 compared to about 1.9 for methane.

Klassen[6] reported an experimentally determined $G(-C_2H_6)$ of 3.3 in good agreement with the value 3.85 reported in Table V at 27% conversion. His values for $G(C_3H_8)$ and $G(n\text{-}C_4H_{10})$ were about three times those in Table V. This probably reflects the difference in per cent conversion of the starting material. Results in Table IV are for conversions of 3.2–74.5% if $G(-C_2H_6) = 3.8$.

The intermediate size hydrocarbons (C_{10}–C_{18}) constituted 50% of the total products. The polymer was 37%; *n*-butane, 8%; methane, 2%; and propane was about 1.6%. The chromatogram of the intermediate size hydrocarbons was like that from methane radiolysis, and the average size is an estimate.

Ethylene, which can polymerize by a chain reaction, would be expected to have a considerably higher *G* value for polymer production. It was found, as shown in Tables VI and VII, that $G(-C_2H_4$ to polymer$) = 4.3$ in a 0.2 mol % solution of ethylene in liquid argon. The polymer was 53% of the product; C_{10}–C_{18}, 26%; methane, 2%; ethane, 5%; propane, 3%; *n*-pentane, 7%; and *cis*-2-butene, 6%. The polymer is very similar to that produced from methane and ethane. About 1% unsaturation was seen in the nmr spectra, but this may have been present and undetected in the dilute solutions used for spectra in the case of methane and ethane polymer. Spectra of the ethylene polymer were run neat.

Table VI. Ethylene–Argon Solutions

Mol % C_2H_4	Dose, Mrad	*G*- (polymer)	Mol wt, g	Av formula
0.46	1.0	0.76	296	$C_{21}H_{44}$
0.47	12.5	0.64	327	$C_{23}H_{46}$[a]
0.67	1.0	0.54	289	$C_{21}H_{42}$
1.13	1.0	0.72	294	$C_{21}H_{44}$

[a] $CH_3:CH_2:CH:C{=}CH = 4:5:7:0.25$; bp 130–160° dec; mp = −114° (broad); n^{25}_D 1.5419; $P_{23}{}^{\circ} = 0.811$ g/cc.

Discussion

A. Facts. The facts about the polymerization of methane appear to be as follows.

(1) Solid methane at 77°K yields polymer of mean composition $C_{20}H_{40}$ which is highly branched and particularly stable thermodynamically.[4f]

Table VII. Ethylene–Argon Solutions

Product	*G*(product)	
Methane	0.35	
Ethane	0.41	
n-Butane	0.23	
n-Pentane	0.023	
tert-2-Butene	0.007	
c-2-Butene	0.024	
n-Hexane	0.006	
tert-2-Pentene	0.005	
c-2-Pentene	0.003	
3-Methylhexane	0.006	
1-Hexene	0.003	
tert-2-Hexene	0.018	
c-2-Hexene	0.008	
Methyloctane	0.001	
n-Octane	0.014	
(C_3–C_{10}) Av $C_{4.5}$	0.35	
(C_{10}–C_{18}) Av C_{10}	0.44	
Polymer	0.43	18 μg expected
Mol % C_2H_4	0.21	0.046
Dose (Mrad)	2.5	0.063
$G(-C_2H_4)$	8.31	0.15

(2) The yield is independent of dose between 1 and 100 Mrad (0.01–1.0% conversion) at 0.32 CH_4 molecules converted to polymer per 100 eV absorbed $G(-CH_4) = 0.32$.[4f]

(3) Light hydrocarbons are produced in wide variety, ethane being the most abundant at $G = 2.1$.[4d,f,5]

(4) In liquid argon solutions a very similar polymer is produced in higher yield, $G(-CH_4) \cong 1.3$, independent of concentration between 0.15 and 15 mol % (*cf.* Table II).

(5) The molecular weight is constant at about $C_{22}H_{42}$ up to about 20 mol % but rises at higher concentrations at around 50 mol %.[3]

(6) The yield $G(-CH_4)$ decreases with increasing concentration above about 15 mol %, falling to 0.5 at 50 and 0.3 at 70 mol %.[3]

(7) At 0.076 mol % concentration, the polymer yield has fallen to 0.017 or $G(-CH_4)$ of 0.3. The lighter hydrocarbon yields have risen to compensate to keep the total $G(-CH_4)$ at about 11 ± 1 (*cf.* Table III). Thus the yield falls at concentrations below 0.15 and above 15 mol % but is relatively constant at intermediate concentrations.

For solid ethane, the facts appear to be as follows.

(1) For pure solid ethane at 77°K, the polymer $C_{23}H_{46}$ forms at $G(-C_2H_6) = 0.2$ yield.[4f]

(2) The polymer was essentially identical with that found from methane, with somewhat fewer methyl groups.

(3) Ethane–argon solutions gave higher yields at $G(-C_2H_6)$ of 2.1 independent of concentration from 0.22 to 0.66 mol % (*cf.* Table IV).

(4) A variety of lighter hydrocarbons were produced similar to the methane case (*cf.* Table V).

For ethylene (*cf.* Tables VI and VII) the facts appear to be as follows.

(1) Polymer yield is higher: $G = 0.43$–0.76, $G(-C_2H_4) = 4.8$–8.4. The variation in *G* seems not to be correlated with dose or concentration.

(2) A wide variety of lighter hydrocarbons are produced: methane, ethane, *n*-butane, and C_{10}–C_{18} range.

(3) The mean molecular composition is about $C_{22}H_{44}$.

The ternary solutions, methane and ethane in argon, methane and ethylene in argon, and ethane and ethylene in argon, gave polymer G values of 0.18, 0.31, and 0.36 for 1 mol % solutions of each of the two hydrocarbons. Again a variety of lighter hydrocarbons was produced.

Propane at 77°K gives polymer[4f] in about the same yield as solid ethane: $G(-C_3H_8)$ of 0.15. The polymer is smaller, $C_{16}H_{32}$.

Finally there is no effect of a sevenfold change in dose rate[4f] in pure solid methane at 77°K.

B. Mechanism. As Davis, *et al.*,[4f] concluded, the solid methane data rather vigorously limit the possible mechanisms to either (case a) processes initiated by a single γ-ray photon which run to completion without further radiation action; (case b) processes in which a steady state between polymer destruction and growth is reached at 1 Mrad or less total dose.

We now can say that one of the case a processes we had suggested earlier,[3] the production of a localized spherical concentration of ions by an Auger shower following an inner shell ionization, probably is eliminated by the ethane and ethylene data. According to this mechanism, the polymer should have about twice the molecular weight of that from methane instead of about the same at twice the yield as observed. The neutral fragments produced by neutralization of the plasma blob should apparently contain an average of nearly two carbon atoms and yet should be just as numerous as those from methane since the ionization potentials for ethane and ethylene are about the same as for methane.

Davis, *et al.*,[4f] showed that the polymer plus the attendant hydrogen released on its formation contains some 9 eV more energy than the methane from which it was produced. Therefore, the mechanism must provide for radiation excitation or ionization.

The fact that the dilute solutions in liquid argon give the polymer appears to eliminate all case a mechanisms, except possibly the Auger which in turn is eliminated by the ethane and ethylene results. The argument is that the neutralization of an ion or deexcitation of an excited state would occur well before as many as 20 methane molecules could react.

Therefore, we turn to accretive processes acting rapidly to establish the polymeric steady state with destruction matching accretion when about 20–25 carbon atoms are incorporated. A conceivable mechanism was suggested by Davis, *et al.*[4f]

$$CH_4 + C_n{}^+H_{2n+1} = H_2 + C_{n+1}{}^+H_{2n+3} \quad (1)$$

followed by neutralization.

The further suggestion was made that the polymer was limited by the energetics of the growth reaction 1. It was suggested that it becomes endothermic for n about 20.

This still seems to be the best approach, although the multiplicity of types of ion molecules reactions, electron transfer, H^- transfer, H_2^- transfer, H_2 transfer, and H atom transfer[4e,5–10] found among the light hydrocarbons cautions against categorical commitment to reaction 1.

Conclusion

It has been shown that the concentrated cloud of reactive species given by Auger processes is probably not necessary to the formation of polymer in the methane–argon system. Instead, a series of rapid reactions between reactive species can produce the polymer. Removal of branched light products and olefins can be accomplished by second ionizations, hydride ion abstraction reactions, and free-radical scavenging reactions. The earlier work of Davis, *et al.*,[4f] can be interpreted in a similar way since rotation and atomic hydrogen diffusion are known to occur at 77°K, the temperature used.

Mass spectrometer and neutral product studies using deuterium and ^{14}C labeled hydrocarbons have shed much light on the wide variety of reactions which occur in the ion molecule chemistry of the hydrocarbons. These include electron transfer, H^- transfer, H_2^- transfer, H_2 transfer, and H atom transfer.[4e,5–10] It therefore is clear that we can hardly claim to have fully elucidated the mechanism of polymer formation in any detail. Whatever the mechanism, however, it appears to exhaust itself energywise when a highly branched saturated hydrocarbon containing about 2 dozen carbon atoms is formed.

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