The current-step method used for coulometrically oxidizing ruthenocene is: Constant current is applied to a rotating platinum electrode (600 r.p.m.) and a shielded electrode. The potential of the rotating electrode is monitored *versus* a reference SCE. When the potential attains a predetermined limit, the constant current is lowered. In this manner the potential is maintained always below a given value. This upper potential limit is selected from the chronopotentiogram run on the system. The number of equivalents of electricity consumed may be easily calculated from the current and time. At different intervals of time, the coulometric oxidation is stopped, the solution allowed to quiet and a chronopotentiogram obtained at the usual platinum electrode used for chronopotentiometric work. The $\tau^{1/2}$ is proportional to the concentration of the electroactive species remaining in the solution. Therefore, a plot of $\tau^{1/2}$ *vs.* number of equivalents from the coulometric oxidation should be a linear relationship if there are no complications to the electrode reaction. Extrapolation of the above plot to where $\tau^{1/2} = 0$ should intersect the axis at a point which corresponds to the number of equivalents of electroactive species which was originally present in the solution.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA]

Radiolysis of Liquid Neopentane[1]

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The products of radiolysis of liquid neopentane by Co^{60} gammas in the range −196 to 50° include, among compounds determinable by gas chromatography, ethane, ethylene, propane, propylene, isobutane, isobutylene, isopentane, neohexane, branched octanes, nonanes, dineopentyl and possibly acetylene. Hydrogen and methane are also found. The major products other than CH_4, C_2H_6, $i\text{-}C_4H_{10}$ and neohexane show minimum G values around −78°. The values of $G(CH_4)$ are higher than those previously reported by Hamashima, Reddy and Burton. Failure of carbon–hydrogen balance is attributed not merely to inaccuracies of analysis but also to possible formation of products higher than decanes. In some experiments, with iodine as solute, the C_8, C_9 and C_{10} products are completely absent, and H_2 and CH_4 are reduced in yield. The other products, C_6 and below, including ethane, are unaffected. Two conclusions regarding the mechanism of radiolysis are that (1) both free-radical and excited molecule reactions appear to be involved, and (2) a significant fraction of the CH_4 may be formed by primary rearrangement decomposition, such as suggested also by the results of Dewhurst on neohexane, who reports that CH_4 production is not completely eliminated by I_2 addition. Ion-molecule reactions may also participate.

Introduction

As background for current studies of the radiolysis of mixtures including neopentane it has been desirable to make a further study of its radiation chemistry over the temperature range −196 to 50°. Values of $G(H)_2$, $G(CH_4)$ and $G(C_2H_6)$ were obtained throughout the entire range and full analyses of the products were made for irradiations at −196, −78 and +30°. The results for $G(CH_4)$ are significantly higher than those previously reported from this laboratory.[3]

Experimental

Materials.—Neopentane (2,2-dimethylpropane), Phillips Research Grade, 99.87 and, more recently, 99.94 mole % pure, was used without purification for most of the temperature-dependence work. For full product analyses, only highly purified material was employed; this same work established that the material used as received was adequate for experiments in which only gaseous products were determined.

Sample Purification and Preparation.—In our earlier work, samples were cooled in the irradiation cells (6 ml. Pyrex ampoules) and degassed while frozen at −78°. Five freezing, evacuating and thawing cycles insured thorough degassing of the samples. Latterly, the following purification was adopted and employed before the degassing cycles.

The neopentane flowed very slowly through a two-foot-long tube packed with coconut charcoal on which bromine was absorbed.[4] The gas then passed through a similar length of pure charcoal and finally through a long phosphorus pentoxide drying tube. About 4 hr. were required to obtain 6 ml. of liquid. This process completely removed previously detected traces of propylene, isobutylene and pentene.

Irradiations.—Irradiation in an underground Co^{60} source was at a rate of about 7×10^{17} ev. ml.$^{-1}$ min.$^{-1}$, as established with the Fricke dosimeter employing an electron density correction of 0.60 for neopentane. Irradiation times varied from 30 to 120 minutes, although 60 minutes was the usual time. For runs from which all the products were examined irradiation times were 120 minutes. The low and high-temperature irradiations were performed in a Dewar flask containing coolant or hot water to give the desired temperature. In some cases, the irradiation had to be interrupted in order to maintain the required temperature.

Analyses.—Hydrogen, methane, ethylene and ethane were extracted by degassing techniques conventional in this Laboratory and were determined with a Consolidated 21-103A mass spectrometer. A Perkin–Elmer 154B Vapor Fractometer was used for the full-product analyses. Products in the range C_2 to C_4 were separated by use of two 2-meter tetraisobutylene (Dx) columns in series at room temperature, C_5 and C_6 products by a 2-meter di-2-ethylhexylsebacate (Bx) column at room temperature and higher products on the Bx column at about 80°.

Preparation of Dineopentyl.—Because the highly branched dimeric products expected were not, on the whole, readily

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[2] To whom requests for reprints should be addressed.

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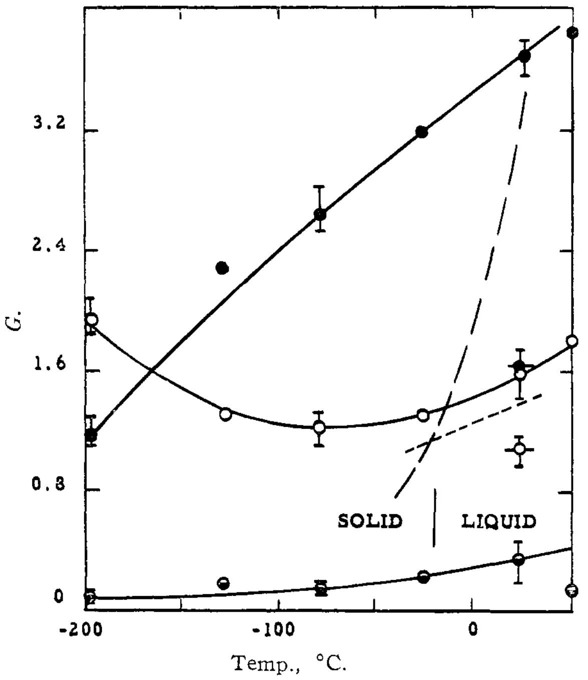

Fig. 1.—Temperature dependence of H_2, CH_4 and C_2H_6 yields; dose rate: *ca.* 7 × 10^{17} ev. $ml.^{-1}$ $min.^{-1}$. From pure C_5H_{12}: ○, H_2; ●, CH_4; ◒, C_2H_6. From I_2–C_5H_{12} solutions: -○-, H_2. Three identical values from I_2–C_5H_{12} solutions: -●-, CH_4. Previous values from this laboratory[3] for pure C_5H_{12}: ---- H_2 and — — — CH_4. Only one determination was made for those points for which no spreads of values are indicated.

obtainable, an authentic sample of dineopentyl, the most important high molecular weight product of the radiolysis, was prepared. A small quantity of di-*t*-butylacetylene kindly supplied by Professor G. F. Hennion was hydrogenated in his laboratory (by Mr. C. A. Lynch) with use of 10% Pd-charcoal catalyst. The product was subjected to micro-fractionation from sodium. The middle cut was chracterized by infrared and no ethylenic bond was found. The freezing point (not accurately determined) was near − 13°. (*Cf.* lit.[5] m.p. = − 13.5°). With a di-2-ethylbenzylsebacate 2-meter, 1/4 inch diameter column (Bx) at a helium inlet pressure of 15 p.s.i. flow rate of 56 ml. $min.^{-1}$, and a temperature of 93°, the retention time of dineopentyl relative to two reference compounds is as follows (corrected for dead volume).

2,2,4-Trimethylpentane	1.00
2,2,5-Trimethylhexane	1.93
Dineopentyl	2.74

Results

Table I shows average product analyses up to C_{10} of samples irradiated at −196, −78 and 30°. The lack of carbon–hydrogen balance is attributable in part to errors inherent in determination of C_8, C_9 and C_{10} compounds by the chromatographic methods employed. Assignments of particular branched octanes and nonanes on the basis of retention times are only tentative; these products have not been further characterized and may contain unsaturation which, if established, would give a much better balance. Some materials above C_{10} may also be produced; the cells appeared greasy after removal of the irradiated neopentane.

Careful examination of the data for major products other than H_2, CH_4 and C_2H_6 shows that the yield of neohexane is an approximately linear function of temperature, while the yields of all the other hydrocarbons studied show minima at an intermediate temperature.

TABLE I

TEMPERATURE DEPENDENCE OF 100 EV. YIELDS FROM NEOPENTANE[a]

Temp. irradiation, °C.	−196°	−78°	+30°	
H_2	1.96	1.23	1.57	
CH_4	1.20	2.63	3.72	
C_2H_6	0.06	0.17	0.33	
C_2H_4	Trace	Trace	<0.01	±20% or 0.01, whichever is larger
C_3H_8	<0.01	<0.01	.01	
C_3H_6	< .01	< .01	.04	
iso-C_4H_{10}	.07	.38	.35	
iso-C_4H_8	.37	.18	.82	
iso-C_5H_{12}	.2	Not determined	.3	±25%
neo-C_6H_{14}	.29	0.69	1.1	
Branched octanes	.15	Not detectable	0.20	
Branched nonanes	.24	0.1	0.50	
Dineopentyl	.60	0.21	1.2	

[a] In all these runs, a very small pip ($G \leqq 0.01$), assignable to either acetylene or CO_2 was observed; experiments necessary to establish the assignment were not performed. With the exception of H_2, CH_4 and C_2H_6 determinations, which are averages of many runs, the yields at +30° are averages of three runs and those at −196 and −78° of two runs.

Figure 1 shows dependence of hydrogen, methane and ethane yields on temperature in the range −196 to 50°. Previous values reported from this Laboratory[3] are shown by dotted lines. In that work the dose rate was 0.2 × 10^{17} $ev.ml.^{-1}min.^{-1}$. Consequently, a few experiments at a dose rate of 0.5 × 10^{17} $ev.ml.^{-1}min.^{-1}$ (averaged over the entire sample) were made but these indicated no effect of radiation intensity on either $G(H_2)$ or $G(CH_4)$. It should be emphasized that our methods of gas collection have been improved since the time of the earlier work. It is particularly probable that not all the methane was extracted in that work; certainly the last traces of methane are extractable from neopentane only with the greatest difficulty.

In an effort to determine whether mode of organization in the solid might have accounted for disagreement with the previous work, the samples were cooled in a variety of ways. Some samples built up by very slow condensation from the vapor at −78° were completely transparent; on radiolysis at that temperature they gave the same results for H_2, CH_4 and C_2H_6 as did the opaque, presumably polycrystalline, samples generally employed.

Figure 1 shows also that dissolved iodine (either ~5 × 10^{-3} *M* or ~5 × 10^{-2} *M*) reduces yields both of hydrogen and, more markedly, of methane. It is notable, however, that methane production is not thereby prevented. The 100 ev. yields of C_2 to C_4 hydrocarbons and neohexane were unchanged

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(5) G. F. Hennion and T. F. Banigan, THIS JOURNAL, **68**, 1202 (1946).

in the presence of iodine; C_8 to C_{10} products were reduced below detectability. However, $G(C_2H_6)$ was not affected within the limits of error, which (as appear from Fig. 1) are relatively large.

Discussion

Requirements of a Mechanism.—A completely satisfactory mechanism for the radiolysis of neopentane would explain not only all the facts related under Results but also the points:

(a) Dewhurst[6] finds that iodine dissolved in the isomeric hexanes inhibits all methane formation except in the single case of neohexane (2,2-dimethylbutane).

(b) Mass spectrometric studies (of gas at $\sim 10^{-6}$ mm.) indicate the major peak to be $(CH_3)_3C^+$ with other large peaks at $C_3H_5^+$, $C_3H_3^+$, $C_2H_5^+$, $C_2H_3^+$ and CH_3^+.

(c) Matheson[7] has examined irradiated neopentane at $-196°$ by paramagnetic resonance technique and suggests that two radical species are observed, namely, $C(CH_3)_3$ and $(CH_3)_3CCH_2$.

(d) The yields reported by Lampe[8] for gaseous neopentane exposed at 27° seem, superficially, unrelated to those shown in this work, as indicated below.

G	Liquid (this work)	Gas (Lampe[8])
H_2	1.57	4.3 ± 1.1
CH_4	3.72	1.8 ± 0.6
C_2H_6	0.33	2.3 ± 0.8

Suggestions of a Mechanism.—Lampe and Field[9] conclude from considerations of electron impact studies (in the gaseous state) that both hydrogen and methane are formed by rearrangement decomposition processes of the $(CH_3)_3C^+$ ion; *e.g.*, $C_4H_9^+ \rightarrow C_3H_5^+ + CH_4$. Such conclusions are, of course, consistent with mass spectrometer patterns. It is unlikely that, in the liquid phase, the hydrocarbon ions can survive even as long as 10^{-13} sec.[10] However, the sequence of

$$C_5H_{12}^+ + e \longrightarrow C_5H_{12}^* \qquad (1)$$

$$C_5H_{12}^* \longrightarrow C_4H_9^* + CH_3 \qquad (2)$$

$$C_4H_9^* \longrightarrow C_3H_5^* + CH_4 \qquad (3)$$

reactions and similar processes (where the asterisk indiscriminately denotes any of a variety of electronically, or even vibrationally, excited states) can be written to account both for all the lower hydrocarbon products in the liquid state and for the failure of iodine completely to eliminate such products. Failure of iodine completely to suppress H_2 formation does not necessarily connote contribution of a primary rearrangement decomposition into ultimate H_2 molecules. Evidence from the radiolysis of other hydrocarbon liquids[11] indicates that the major fraction of primarily produced free hydrogen atoms may be inaccessible to the action of scavenger.

The persistence of methane yield in the presence of iodine in both neopentane and neohexane[4] suggests that molecular symmetry is related to the mode of fragmentation. Such a relation is also suggested by the predominance of the *t*-butyl ion peak in the mass spectra of those compounds.

Mass spectral studies of neopentane[12] with centrally labelled C show that about 47% of the $C_2H_5^+$ produced is labelled. It is consistent with such a finding that the process of C_2H_6 formation involves considerable rearrangement of the neopentane bonds; *i.e.*, not all the C_2H_6 is formed by combination of CH_3 radicals. This view of a method of formation of C_2H_6 is supported also by the studies of Trost and Steacie[13] who give evidence that the entire C_2H_6 yield from excited neopentane (resultant in their case from combination of C_5H_{11} and H) comes from rearrangement decomposition in a single step. Our findings that C_2H_6 formation persists in presence of I_2 is therefore not surprising; $G(C_2H_6)$ would be affected by I_2 addition were any C_2H_6 formed by combination of CH_3 radicals. However, the effect of I_2 on $G(CH_4)$ definitely suggests that CH_3 radicals are present. One possible inference from such results is that at the low free radical concentration prevalent in the system (and because the free CH_3 radicals may be initially "hot") the abstraction reaction

$$CH_3 + C_5H_{12} \longrightarrow CH_4 + C_5H_{11} \qquad (4)$$

is far more probable than any combination with a free radical

$$CH_3 + R \longrightarrow CH_3R \qquad (5)$$

When we examine the effect of temperature on CH_4 yield, it appears reasonable to account for decrease on the basis of competition between the two reactions 4 and 5 where, in the "cage," R would be C_4H_9. The latter reaction in the cage would be favored at low temperature because of the considerable activation energy (*ca.* 10.2 kcal)[14a] of reaction 4. Lampe's high value $G(C_2H_6) \sim 2.3$ in the gas compared to our relatively low value $G(C_2H_6) = 0.33$ suggests that an important contribution to $G(C_2H_6)$ in the gas may be methyl-radical combination.

The effect of temperature on hydrogen yield suggests two processes: one dominant at low temperature but insignificant at higher, the other with opposite temperature characteristics. A convenient model on the basis of which much of the $G(H_2)$ variation may be explained is afforded on the assumption of a progenitor reaction

$$C_5H_{12}^* \longrightarrow C_5H_{11} + H \qquad (6)$$

The H atom so produced may either back-react immediately (and thus be undetected) or escape the cage before it is reduced to thermal velocities. Its subsequent experience depends on the temperature.

It is reasonable to infer from paramagnetic resonance studies of Livingston and others that H atoms do not survive free for any significant time in solid

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systems at liquid air temperatures.[7,15] Production of H_2 at such low temperatures[16] suggests that

$$H + H \longrightarrow H_2 \qquad (7)$$

H atoms may find each other with high probability even at liquid air temperature.

In order to understand the decrease in H_2 yield at intermediate temperatures, we assume that the probability of some reaction of low activation energy, *e.g.*, addition of H atom to a double bond (*cf.* the drops in isobutylene yield and corresponding rise in isobutane at such temperature), increases with temperature. Were there no compensatory process, the effect of increased temperature would be to reduce $G(H_2)$ to a value approximating the yield in the presence of iodine scavenger.[11]

As the temperature rises, a new source of H_2, the reaction

$$H + C_6H_{12} \longrightarrow H_2 + C_6H_{11} \qquad (8)$$

which has an activation energy of *ca.* 9.2 kcal.,[14b] becomes increasingly important so that H_2 yield tends to increase, as found.

Critique of Suggested Mechanism.—The mechanism outlined in the preceding section is consistent with, or accounts for, the results and the findings outlined in the section entitled Requirements of a Mechanism with the notable exception that we have offered no detailed suggestions as to mechanism of formation of intermediate hydrocarbons. Furthermore, possible contribution of ionic reactions, *e.g.*, of the interesting type possible in liquids[17]

$$M^{+}\cdot M + e \rightarrow \text{products} \qquad (9)$$

is completely ignored. Reactions of type 9 may be particularly important at low temperatures and might account both for increased $G(H_2)$ and for increased $G(C_8)$, $G(C_9)$ and $G(C_{10})$ under such conditions. It is interesting to note in connection with such a proposed process 9 that iodine has no effect on $G(\Sigma C_4)$, *i.e.*, G of total C_4 products, or on G (neohexane) and that $G(\Sigma C_4)$ is approximately the same as G (neohexane) at all temperatures.

Acknowledgments.—The authors are greatly indebted to Professor G. F. Hennion who provided both the material and the technique for synthesis of authentic dineopentyl and to Mr. C. A. Lynch who actually synthesized it.

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Relation Between Methyl Affinities and Conformation of the Conjugated Dienes

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Methyl affinities of 1,2-dimethylenecyclobutane, 1,2-dimethylene-3-methylcyclopentane and 1,2-dimethylenecyclohexane were determined. The first two dienes were shown to be 2.3 and 3.2 times as reactive as butadiene or isoprene, whereas the last compound is only one-half as reactive as butadiene. The relatively low reactivity of the latter compound is explained by the lack of coplanarity of its vinyl groups. On the other hand, the unusually high reactivity of the first two compounds calls for a new hypothesis. It is suggested tentatively that the co-planar *cis*-conformation of the vinyl groups introduces considerable steric strain which is released in the transition state as a result of the change from the sp_2 to sp_3 configurations. This may lower the activation energy of the process and increase the respective methyl affinity. Moreover, such an explanation accounts for the higher reactivity of the cyclopentane derivative than that of the cyclobutane derivative since the reactive CH_2 centers are more closely placed in the former compound than in the latter.

Kinetic studies of the addition of methyl radicals to butadiene-1,3, isoprene and 2,3-dimethylbutadiene demonstrated a very close similarity in the reactivities of these hydrocarbons[1,2] (see Table I). The observed methyl affinities, *i.e.*, the relative rate constants of methyl radical addition, can be actually accounted for quantitatively by considering the localization energy of butadiene and the effects of hyperconjugation.[3,4]

Conjugated dienes may exist in two conformations, namely a *cis* conformation in which both vinyl groups are located on the same side of the C–C bond, and the *trans* one with the vinyl groups located on the opposite sides of this bond. Spectroscopic studies of butadiene[5] showed that the *trans* conformation is preferred for this hydrocarbon and the difference in energy levels of the *cis*- and *trans*-conformations was estimated to be 2.3 kcal./mole. Hence, in the equilibrium established at 65° more than 97% of that compound is present in the *trans* rotational form. On the other hand, recent spectroscopic studies of Nikitin and Yakovleva[6] lead them to conclude that the preferred conformation of isoprene is *cis*, which means that the latter rotational isomer forms at 65° the bulk of this hydrocarbon.

If the assignments of these conformations are correct, then the kinetic results, mentioned at the

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