TABLE X

A comparison of spin densities for the lowest triplet state of pyrrole, pyridine, pyrimidine and purine; OS refers to values obtained using the open shell method and VO to value obtained from the virtual orbitals generated in the ground state calculation.

Position	Pyrrole		Pyridine		Pyrimidine		Purine	
	OS	VO	OS	VO	OS	VO	CS	VO
1	0.105	0.094	0.212	0.228	0.255	0.235	0.846	0.416
2	.773	.661	.366	.353	.137	.190	.002	.132
3	.174	.292	.339	.339	...	...	.139	.210
4	...	...	.369	.390	.428	.432	.106	.277
5			...	...	.496	.472	.003	.261
6					...	...	.856	.228
7							.016	.116
8							.007	.200
9							.027	.161

TABLE XI

A comparison of spin densities for the doublet anions of pyrrole, pyridine, pyrimidine and purine; OS refers to values obtained using the open shell method and VO to values obtained from the virtual orbitals generated in the ground state calculation.

Position	Pyrrole		Pyridine		Pyrimidine		Purine	
	OS	VO	OS	VO	OS	VO	OS	VO
1	0.113	0.094	0.200	0.228	0.187	0.181	0.178	0.167
2	.328	.317	.079	.120	.0	.0	.017	.019
3	.116	.136	.082	.071	...	...	.088	.118
4	...	...	.476	.390	.313	.318	.061	.067
5			...	...	.0	.0	.0	.003
6					...	...	.561	.444
7							.0	.0
8							.048	.102
9							.045	.067

densities may be obtained from the ground state determination. This has been done and the results are compared with those spin densities calculated when the open-shell procedure is used. In the latter case no explicit reference (except for geometry, as indicated above) is made to the ground state of the system of interest. Tables X and XI list these values.

Only scant experimental evidence is available so that it is not possible to make a judgment as to which method is to be preferred. Carrington and dos Santos-Veiga, in a recent electron spin resonance study of the anions of N-heteroaromatics,[37] point out that both pyridine and pyrimidine anions appear to dimerize. They state that for the case of the pyridine system, reaction occurs at the four position, which is the result that would be predicted on the basis of the present calculation.

Using the definition of electron density set down in the last section, and using the two methods outlined above, we have also calculated the electron densities of the lowest triplet and doublet anions of these molecules. These results are found in VIII and IX.

For the case of the electron density, it is seen that both methods predict the same relative reactivity. In the case of the spin densities, reasonable agreement between the two methods is evident except for the purine triplet where rather large differences appear.

Acknowledgment.—We wish to acknowledge a generous grant of Univac 1105 time made available by the Illinois Institute of Technology, and several useful discussions with Dr. R. L. Flurry and Mr. D. James of this department.

(37) A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN]

Solute–Solvent Interactions in the Radiolysis of Alkyl Halide–Pentane Solutions[1]

BY PAUL R. GEISSLER AND JOHN E. WILLARD

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The *G* values for production of methyl, ethyl, propyl and pentyl radicals by the radiolysis of 0.25 mole % solutions of iodine in pentane are reduced by the presence of methyl iodide, ethyl iodide or normal propyl bromide at concentrations in the range of 1%, except for the radical representing the hydrocarbon fragment of the alkyl halide. The latter is produced with high yield. The total *G* (radicals) is increased from 8.2 to about 11.6 by the halide additives. The presence of normal propyl chloride does not produce these effects. Studies of the fate of $C^{14}H_3$ radicals produced in the radiolysis of $C^{14}H_3I$ solutions in pentane and of the fate of I^{131} from similar $C_2H_5I^{131}$ solutions have been used to examine further the solute–solvent interactions during radiolysis. The evidence indicates that the reaction $RI + e^- \rightarrow R + I^-$ must play a significant role in such systems and supports the conclusion that neutralization of RH^+ ions by negative ions is less apt to lead to radical production than neutralization by electrons. Electron capture and any other indirect processes which may lead to $C^{14}H_3$ production during radiolysis of solution of $C^{14}H_3I$ in pentane increase in yield with increasing concentration below about 0.8 mole % and remain constant at higher concentrations, indicating that all available electrons and other radical producing species react with the halide at this concentration. Iodine production occurs during the radiolysis of ethyl iodide pentane solutions in which only 10% of the energy is absorbed by the ethyl iodide. This reflects solute–solvent interactions since *G* (radicals) in the radiolysis of pentane is 8.2 while $G(^1/_2I_2)$ in the radiolysis of C_2H_5I is 4.2.

Introduction

There are two significant reasons for studying the radiolysis of dilute solutions of alkyl halides in hydrocarbons. One is the possibility that such studies may yield evidence for the reaction

$$RI + e^- \longrightarrow R + I^- \qquad (1)$$

thus supporting the concept that electrons ejected from solute molecules escape from the parent positive ion rather than returning immediately to it under the influence of the coulombic field. The second reason is to explore reactions other than (1) which may result from solvent–solute interactions, for the purpose of gaining improved understanding of the mechanism of hydrocarbon radiolyses. The first goal was initially suggested and attempted by Williams and Hamill[2] using several solutes with

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(1) (a) Presented before the Division of Physical Chemistry at the September 1961 meeting of the American Chemical Society at Chicago, Illinois; (b) Additional details of this work are given in the Ph.D. thesis of Paul R. Geissler, University of Wisconsin, 1962, available from University Microfilms Ann Arbor, Michigan.

(2) R. R. Williams and W. H. Hamill, *Radiation Research*, **1**, 158 (1954).

high electron affinities in cyclohexane and other solvents. The electron capture process has been discussed by Magee and Burton[3]; the properties of sub-excitation electrons have been considered by Platzman[4]; and both Schuler[5] and Forrestal and Hamill[6] have made further studies of the radiolysis of alkyl iodide–cyclohexane solutions. In these it has been emphasized that the alkyl halide solute may influence the radiolysis by reactions other than (1) including

$$RI + R' \longrightarrow R'I + R \qquad (2)$$

$$RI + H \longrightarrow R + HI \qquad (3)$$

$$RI + RH^+ \longrightarrow RI^+ + RH \qquad (4)$$

The authors[3,6] have also pointed out that if reaction 1 occurs with high probability hydrocarbon ions which would be neutralized by free electrons in the absence of solute

$$RH^+ + e^- \longrightarrow RH \qquad (5)$$

$$\hookrightarrow R + H \qquad (6)$$

may, in the presence of solute, be neutralized by negative ions which is a less exothermic process and so may lead to a different chemical fate of the ion being neutralized. In all the studies reported the nature of the elementary steps has been deduced by analysis for the hydrogen, hydrocarbons or iodides formed from the mixture, or analysis for labelled iodides formed in the presence of $I_2(I^{131})$ added as a scavenger. In the work reported below we have investigated the specific fate of the components of the dilute solute by studying the C^{14}-labelled products formed using $CH_3I(C^{14})$ as solute and the I^{131}-labelled products using $C_2H_5I(I^{131})$ solute in pentane. We have also determined the effect of dissolved alkyl halides on the *G* values of radicals formed during the radiolysis of pentane solutions.

Experimental

γ-Irradiations.—Samples for irradiation were contained in annular glass vessels which fit closely around a 200-curie cobalt-60 source of the design previously described,[7] or in thin glass bulbs with a radius of 3 mm., which could be reproducibly positioned next to the source. The samples in annular vessels were usually about 3 ml. in volume and in the bulbs were 0.2 ml. The latter were used for gas chromatographic analysis, and the former for determination of $I_2(I^{131})$ organic uptake.

The dose rate for both types of sample containers during the period of this work was approximately 10^{18} e.v. g.$^{-1}$ min.$^{-1}$. The exact values of the dose rates were determined by use of ferrous sulfate dosimetry using 15.6 as the *G* value for ferric ion production and a value of 2160 l. mole^{-1} cm.$^{-1}$ at 3050 Å. for the molar absorbancy index of ferric ion in the dosimetry solutions at 22.5°. From the ferrous sulfate determinations the dose rates in the pentane solutions were calculated by applying corrections for electron density. Less than 1% of the total absorbed energy was absorbed by the photoelectric effect even in the most concentrated iodide solutions used. All sample irradiations were carried out at ambient temperatures.

Sample Preparation.—The methods of purification of alkyl halides have been described earlier.[8,9] Phillips "Pure Grade" pentane was purified by prolonged mechanical stirring with concentrated sulfuric acid, washing with aqueous bicarbonate, drying, and distillation through a 91-cm. Todd distillation column packed with glass helices. Gas chromatographic analyses of purified reagents showed no impurities above 0.05 mole %. In the experiments determining iodine production in ethyl iodide–pentane solutions, the pentane was used as received without further purification.

Alkyl iodides labelled with I^{131} were prepared by photolyzing the alkyl iodide in the presence of $I_2(I^{131})$ with 2537 Å. light. The tagged alkyl iodide was purified and collected by trapping it on a cooled firebrick column as it came off a gas chromatographic column. Carbon-14 labelled methyl iodide was obtained from Nuclear of Chicago and was purified in the same manner as the I^{131} labelled alkyl iodides. $I_2(I^{131})$ was added to samples by fusing $NaI(I^{131})$ with $K_2Cr_2O_7$ crystals under vacuum and distilling the I_2 formed through a P_2O_5 column.

All samples were prepared and sealed under vacuum.

Product Analysis.—Radiolysis products were separated using gas chromatographic techniques. The I^{131} labelled products were determined with a well type scintillation crystal arranged so that the effluent from the chromatography column flowed through a finger in the well. The C^{14}-labelled products were determined with an internal gas flow proportional counter. The detectors were calibrated with known amounts of the radioactive reactant for both the experiments with $CH_3I(C^{14})$ and with $C_2H_5I(I^{131})$.

Total production of I^{131} labelled alkyl iodides in the radiolysis of alkyl halide–pentane solutions with $I_2(^{131})$ present was determined by the uptake of I^{131}. This was done by counting carbon tetrachloride solutions of the irradiated sample, both before and after they were extracted with aqueous reducing solutions. From the percentage of total I^{131} activity in the extracted solution and the measured amount of iodine present in the original sample, the total yield of labelled iodides was calculated. The yields of the individual iodides were obtained by multiplying this total by the fraction of the total chromatographic peak area represented by each iodide.

Iodine production in ethyl iodide–pentane solutions was measured by determining the iodine concentration with a Beckman DU Spectrophotometer. This was done after each of several periods of irradiation, since the sample could be irradiated and analyzed without destroying it. Wave lengths of maximum absorption for solutions of iodine in ethyl iodide–pentane mixtures and the molar absorbancy indices at those wave lengths were determined using weighed amounts of iodine in the solutions and their absorption spectra obtained with a Cary Model 11-MS recording spectrophotometer. For the solutions studied these were 890 l. mole^{-1} cm.$^{-1}$ at 5180 A. for 0 mole % ethyl iodide, 900 at 5010 for 9.7%, 940 at 4980 for 12.5%, 1020 at 4900 for 25.5% and 1200 at 4820 for 58.8%.

Results and Discussion

The types and yields of radicals formed by the radiolysis of liquid pentane have been investigated by Wagner[10] using an electron beam which gave an absorbed dose of about 7×10^{21} e.v. g.$^{-1}$ min.$^{-1}$. From the analysis of products he estimated the relative yield of the different hydrocarbon radicals produced, assuming that each type of radical–radical combination had equal probability except for differences in concentration. In line 1 of Table I we have listed "*G* values" calculated by multiplying Wagner's fractional yield for each radical by the total *G*(radicals) = 8.2 obtained in the present work from observing the rate of entry of radioactive iodine into organic combination as a function of dose. Line 2 of Table I gives the *G* values for the individual radicals as determined in our work from gas chromatographic analysis of the alkyl iodides formed during radiolysis of pentane in the presence of $I_2(I^{131})$. The similarity

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(3) J. L. Magee and M. Burton, *J. Am. Chem. Soc.*, **73**, 523 (1951).

(4) R. L. Platzman, *Radiation Research*, **2**, 1 (1955).

(5) R. H. Schuler, *J. Phys. Chem.*, **61**, 1472 (1957).

(6) L. J. Forrestal and W. H. Hamill, *J. Am. Chem. Soc.*, **83**, 1535 (1961).

(7) R. F. Firestone and J. E. Willard, *Rev. Sci. Instr.*, **24**, 904 (1953).

(8) E. O. Hornig and J. E. Willard, *J. Am. Chem. Soc.*, **79**, 2429 (1957).

(9) R. J. Neddenriep and J. E. Willard, *J. Phys. Chem.*, **65**, 1206 (1961).

(10) C. D. Wagner, *ibid.*, **64**, 231 (1960).

TABLE I

G VALUES OF RADICALS PRODUCED IN THE RADIOLYSIS OF *n*-PENTANE WITH AND WITHOUT SOLUTES, AS DEDUCED FROM FORMATION OF RR, RI^{131} AND $C^{14}H_3R^a$

	RX solute, mole %	$I_2(I^{131})$, mole %	Radicals indicated by compounds observed										Total *G* (radicals)
			CH_3	C_2H_3	C_2H_5	iso-C_3H_7	*n*-C_3H_7	sec-C_4H_9	*n*-C_4H_9	2-C_5H_{11}	3-C_5H_{11}	1-C_5H_{11}	Others	
1	Pure pentane^b		0.36	..	1.07	..	0.98	..	0.18	2.85	1.40	1.34	..	
2	0.00	0.25	0.50	..	1.16	0.06	.84	..	.08	2.8	1.4	1.4	..	8.2
3	CH_3I, 0.1	.25	3.0	..	0.66	.04	.42	0.04	.07	2.4	1.3	0.92	..	8.8
4	CH_3I, 1.2	.25	6.3	..	0.60	.04	.38	.05	.08	2.1	1.1	.95	..	11.6
5	C_2H_5I, 0.1	.25	0.18	0.02	3.3	.04	.61	.03	.09	2.3	1.1	.9	0.24	8.8
6	C_2H_5I, 1.2	.25	.28	.05	6.7	.04	.35	.04	.07	1.9	0.95	.61	0.6	11.6
7	*n*-C_3H_7Br, 1.2	.25	.32	.03	0.74	.05	4.6	.09	.10	2.2	1.2	1.0	0.4	10.8
8	*n*-C_3H_7Cl, 1.2	.25	.67	.04	1.1	.07	1.1	.04	.10	3.1	1.4	1.2	..	8.8
9	$CH_3I(C^{14})^c$	.00	.12^d (+4.6 CH_4)	..	0.032	..	0.024	..	..	0.055	0.025	0.045	..	
10	$C_2H_5I(I^{131})^e$	.00	0.041	..	Parent	..	0.065	..	..	0.59	0.29	0.25	..	

[a] Each value listed is the average of two independent determinations except for the 0.1% C_2H_5I solution where only one determination was made, and the $C_2H_5I(I^{131})$ solutions where the data are the average of some 15 determinations at 5 concentrations of 0.3 to 10 mole %. All experiments were done at dose rates of 1–5 × 10^{18} e.v. g.$^{-1}$ min.$^{-1}$ Total doses varied from 2 to 75 × 10^{19} e.v. g.$^{-1}$. [b] Fractional radical yields of Wagner[10] multiplied by *G*(total radical in I_2 solution = 8.2) obtained in this work. [c] The numbers on this line indicate the yield of the compound formed by reaction of $CH_3(C^{14})$ with the radical shown at the top of the column. In addition to these products $CH_4(C^{14})$ was formed with $G = 4.6$. *G*(total C^{14} products) = 5.2. The values were obtained from the plateaus of Figs. 1 and 2. Dose rates were 1 × 10^{18} e.v. g.$^{-1}$ min.$^{-1}$; total dose 25 × 10^{19} e.v. g.$^{-1}$. [d] Assuming only one CH_3 from $CH_3I(C^{14})$ per C_2H_6 molecule. [e] Dose rates 1 × 10^{18} e.v. g.$^{-1}$ min.$^{-1}$; total dose 75 × 10^{19} e.v. g.$^{-1}$.

in ratio of radicals as deduced from analysis for hydrocarbons in the radiolysis of pure pentane and analysis for alkyl iodides in the radiolysis of pentane–iodine mixtures is striking, but possibly fortuitous in view of the assumptions inherent in the estimates from the experiments with pure pentane.

The value of 8.2 obtained in this work for $G(^1/_2I_2)$ incorporation in organic combination is essentially the same as the value of 8.4 obtained spectrophotometrically[11] for the disappearance of I_2 during the radiolysis of pentane solutions. If the identity of these values is correct it indicates formation of HI in this system is negligible.

Comparison of lines 3–6 of Table I with line 2 shows that the presence of as little as 0.1% alkyl iodide in a 0.25% I_2 pentane solution during radiolysis raises the total radical yield. The change is the result of a large increase in the yield of the radical associated with the alkyl halide, coupled with a decrease in the yields of other radicals. This effect is more pronounced with 1.2% alkyl iodides but a single experiment with 6.7% C_2H_5I suggests that it approaches saturation in this range since the values at this level are similar to those at 1.2%. Addition of propyl bromide, line 7, has an effect similar to addition of the iodides but somewhat smaller, while added propyl chloride causes little or no effect.

It is apparent from the lowering of the yields of radicals formed from the solvent, noted above, that alkyl iodides and bromides are able in some manner to affect the course of reactions initiated by energy absorbed in the solvent. This is further emphasized by the fact that when the solute is $C_2H_5I(I^{131})$ the *G* values of labelled products seem to be independent of the concentration of the solute over at least a range from 0.3 to 10% when calculated on the basis of total energy absorbed in the system, but increase with decreasing concentration of solute when calculated on the basis of energy absorbed in the solute. When the solute is $CH_3I(C^{14})$ a similar independence of concentration is shown above about 0.75% (Figs. 1 and 2). Thus the reactions of the solute must result primarily from energy absorbed in the solvent rather than the solute (if the *G* values of CH_4 of Fig. 1 were calculated on the basis of energy absorbed only by the CH_3I they would lie in the range of 1300 to 130).

It is probable that the effects of the alkyl halide solutes are due to one or more of the reactions 1–6 noted in the Introduction. Reaction 2 cannot account for a major part of the observed effect. It would cause an increase in the yield of radicals derived from the alkyl iodide, but could not cause the observed increase in the total radical yield. Likewise reaction 3 alone cannot account for the data. There is no apparent way in which this reaction could cause the observed lowering of the yields of pentyl, propyl and methyl or ethyl radicals below the yields of these species from I_2–pentane solutions without added alkyl halide. Reaction 1, electron attachment, and reaction 4, charge transfer, are capable of explaining this observation, as will be discussed further in a later section.

The production of thermal hydrogen atoms in the radiolysis of liquid pentane has been reported by Hardwick[12] to have a *G* value of 4.25. This sets an upper limit of 4.25 on the *G* of reaction 3. The *G* of CH_3 radicals produced from 1.2% CH_3I in the I_2–pentane solutions of Table I is 6.0. This may be deduced from the fact that the total *G* of CH_3 is 6.3 in this solution while the *G* of CH_3 formed in the absence of CH_3I but in the presence of 1.2% C_2H_5I (*i.e.*, formed from the pentane solvent) is 0.28. A similar value (6.1) for

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(11) E. N. Weber, P. F. Forsyth and R. H. Schuler, *Radiation Research*, **3**, 68 (1955).

(12) T. J. Hardwick, *J. Phys. Chem.*, **66**, 101 (1961).

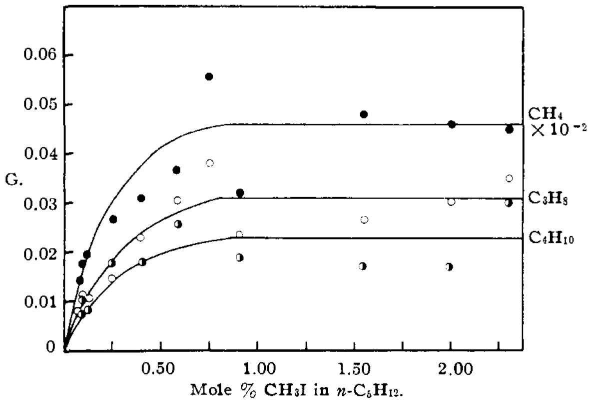

Fig. 1.—Yields (molecules per 100 e.v. absorbed) of methane, propane and butane formed by incorporation of CH_3 from $CH_3I(C^{14})$ during the radiolysis of solutions of $CH_3I(C^{14})$ in n-C_5H_{12}. The values for CH_4 are plotted for an ordinate scale of 0 to 6 while the scale for C_3H_8 and C_4H_{10} is 0 to 0.06.

radicals produced from the solute is obtained by subtracting the value for ethyl radicals formed in 1.2% CH_3I solutions (0.6) from the value for ethyl radicals formed in 1.2% C_2H_5I solutions. Reactions which do not involve hydrogen atoms must therefore account for a *G* of radicals formed from the alkyl iodide of at least 1.7. (It is interesting to note from Table I that the *G* of C_2H_5 from 0.1% C_2H_5I (3.3–0.66) and the *G* of CH_3 from 0.1% CH_3I (3.0–0.18) in I_2–pentane solutions are equivalent to each other, though lower than the corresponding values in 1.2% solutions.)

Reaction 4, $RH^+ + RI \rightarrow RH + RI^+$, is energetically possible and at first appears as an interesting possibility for explaining the observed facts if it were followed by

$$RI^+ + e^- \longrightarrow R + I \qquad (7)$$

This sequence has the qualitative features of reducing the yield of pentyl radicals and fragments of the pentyl chain which would result from the direct neutralization of RH^+ by e^- while at the same time producing the radicals characteristic of the alkyl halide. The impotency of C_3H_7Cl in affecting the results (Table I, line 8) is also consistent with this mechanism since its ionization potential (10.7 e.v.)[13] is higher than that of n-C_5H_{12} while the ionization potentials of propyl bromide and the iodides are lower. However, the reaction (4) charge neutralization mechanism is not consistent with the quantitative change in radical yields caused by the addition of the alkyl halide to the I_2–pentane solutions. In the absence of added alkyl iodide the *G* of radicals formed from the pentane is 8.2. In the presence of 1.2% alkyl iodide the *G*(radicals) is 11.6 of which 6 is due to radicals from the alkyl halide and 5.6 is due to radicals produced from the pentane. Thus the alkyl halide has resulted in a decrease of $8.2 - 5.6 = 2.6$ in radicals produced from the pentane and an increase of 6 due to radicals from the additive. There seems to be no plausible combination of charge transfer and neutralization steps such as (4) and (5) which would yield a larger number of alkyl radicals of the alkyl halide than the decrease in the number of pentyl and pentyl fragment radicals. The possibility remains, however, that reaction 4 is responsible for the decrease in yield of radicals produced from the solvent while a combination of reactions 1, 2, 3, 4 and 7 is responsible for the increased yield of radicals characteristic of the solute.

It should be noted that in these comparisons of different suggested mechanisms we are ignoring reactions of charge transfer, electron attachment or H atom attack on I_2 molecules. This is done because the observed effects which we are discussing are all for identical 0.25 mole % I_2 in pentane solutions which differ only in that some contain added alkyl halide while others do not.

The only mechanism which is independently able to explain all of the available experimental observations is the one involving electron attachment (reaction 1), coupled with the concept that RH^+ ions are less apt to form radical fragments when neutralized by X^- or RX^- than when neutralized by a free electron. The yield of pentyl radicals and pentane fragment radicals is lowered because the neutralization energy is reduced by the electron affinity of the negative ion plus loss in energy suffered by the negative ion in moving toward the positive ion in the liquid medium.[6] The fact that the yield of such radicals is not eliminated may be due to the fact that there is still an appreciable probability that this remaining energy will distribute itself in such a way as to cause bond rupture or it may be due to the fact that some radical formation occurs from excited molecular states rather than as a result of charge neutralization.

The *G* values of 6 for CH_3 formation from 1.2% CH_3I and for C_2H_5 formation from 1.2% C_2H_5I imply, according to this mechanism, that the *G* of e^- formation in pentane solvent is at least 6. This is about twice the most common values observed in gas phase systems but cannot be excluded on the basis of available evidence for this liquid phase system where the probability that the Compton electrons will lose energy by ionization rather than excitation may be appreciably different than in the gas phase.

Molecular iodine would also be expected to undergo electron attachment. If the electron attachment mechanism discussed in the preceding paragraph is correct, the 0.25 mole % I_2 does not compete 100% effectively for electrons with RI present at 0.1 mole %. Since there seems to be no increase in effectiveness of added RI in the concentration range from 1.2 to 6.7% it is implied that it is 100% effective in capturing electrons above a concentration of about 1%. This is also indicated, as will be discussed further, by the data of Figs. 1 and 2.

Line 7 of Table I shows that 1.2% n-C_3H_7Br has the same qualitative effect as the alkyl iodides in increasing greatly the yield of the radical characteristic of the additive and in lowering the yields of pentyl radicals and radicals formed by breaking the carbon–carbon bonds in pentane.

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[13] F. H. Field and V. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957, p. 112.

The changes in yields are, however, not quite as large as caused by the iodides. This may indicate that the rate constant for capture of electrons by C_3H_7Br is not as large relative to capture by I_2 as in the case of the iodides. Addition of 1.2 mole % n-C_3H_7Cl to a 0.25% I_2–pentane solution (Table I, line 8) does not decrease the yields of the radicals derived from pentane and does not increase the yield of C_3H_7 radical. Thermodynamically the reaction $RX + e^- \rightarrow R + X^-$ is possible for each of the primary halides, the approximate endothermicity being 0.9, 0.4, and 0.4 e.v., respectively, for RI, RBr and RCl. As suggested earlier,[6] it appears that the kinetics of electron attachment to the alkyl chlorides may be unfavorable. This point of view is supported by the fact that the appearance potentials of I^-, Br^- and Cl^- from the methyl halides are 0, 0 and 10 e.v., respectively.[14]

The experiments discussed thus far have all dealt with pentane solutions containing 0.25 mole % I_2. Lines 9 and 10 of Table I present data for experiments in the absence of I_2 with dissolved $CH_3I(C^{14})$ and with dissolved $C_2H_5I(I^{131})$. In each case the only products determined were those formed from the labelled species. The total G of C^{14} labelled products from $CH_3I(C^{14})$–pentane solutions at concentrations above about 1 mole % was 4.9. Of this, 4.6 was due to $CH_4(C^{14})$ and the remainder to products attributable to reaction of $CH_3(C^{14})$ with radicals formed from pentane. For identical experiments with C^{14} labelled CH_3I in the presence of 0.25 mole % I_2 the CH_4 yield drops to 0.3 and the yields of the other radicals detected (CH_3, C_2H_5, and C_3H_7) drop to about half the values of line 9, Table I. Figures 1 and 2 show that at concentrations of $CH_3I(C^{14})$ below about 0.75 mole % the G values for each of the C^{14} labelled hydrocarbon products drops toward zero with decreasing concentration of CH_3I.

These observations are consistent with the mechanism dependent on electron attachment by the alkyl halide, discussed in earlier paragraphs. In the absence of added I_2 the CH_3 radicals formed by dissociative electron capture must be consumed either by abstraction of hydrogen from the solvent or by combination with other radicals. For the dose rates used in this work, it may be estimated[1b] that if G of radical formation is 10 and if all radicals are eventually removed by combination with other radicals on their first collision with such a radical, then the steady state radical concentration is about 1 radical in every 10^9 pentane molecules. Using this value, the ratio of $G(CH_4)$ to G for the products of radical combinations may be estimated for the reactions

$$CH_3 + C_5H_{12} \longrightarrow CH_4 + C_5H_{11} \quad (8)$$

$$CH_3 + R \longrightarrow CH_3R \quad (9)$$

by

$$\frac{G(CH_4)}{G(CH_3R)} = \frac{\text{Rate of 8}}{\text{Rate of 9}} = \frac{k_8(CH_3)(C_5H_{12})}{k_9(CH_3)(R)}$$

At 25° k_8 has been shown[15] to be 121 l. mole^{-1} sec.$^{-1}$ in the gas phase. If we take 2×10^{10} l. mole^{-1} sec.$^{-1}$, the rate constant for the combined rates of disproportionation and recombination of ethyl radicals in the gas phase,[16] as an approximation of k_9, and assume that k_8 and k_9 will be equally affected by differences between the gas and liquid phases, then $G(CH_4)/G(CH_3R) \approx 6$. These estimates indicate that it is not implausible that a competition between hydrogen abstraction and radical combination occurs in this system.

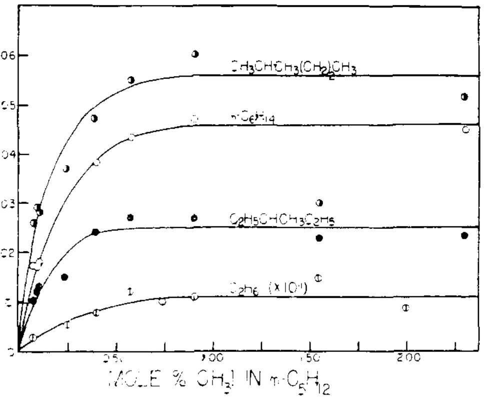

Fig. 2.—Yields (molecules per 100 e.v. absorbed) of ethane, 3-methyl pentane, normal hexane and 2-methyl pentane formed by incorporation of CH_3 from $CH_3I(C^{14})$ during the radiolysis of solutions of $CH_3I(C^{14})$ in n-C_5H_{12}.

The residual yield of $CH_4(C^{14})$ (G = 0.3) and other C^{14} products in the presence of added iodine indicates a small contribution from processes which are not sensitive to scavenging. Possible responsible reaction steps may include: $CH_3I + e^- \rightarrow CH_3 + I^-$, with sufficient energy from the electron attachment process remaining with the CH_3 to allow it to react as a hot radical on one of the first few collisions; and CH_3I^- formed without dissociation, reacting with RH^+ to form RCH_3+HI or a different hydrocarbon and in alkyl iodide.

The fact that the total yield of C^{14} labelled products from the $CH_3I(C^{14})$ is 4.9 as contrasted to the $G(CH_3)$ = 6.3 deduced[17] from the experiments with I_2–pentane solutions containing added C_2H_5I or CH_3I is presumably due to the back reaction $CH_3 + I \rightarrow CH_3I$, involving iodine atoms which have been dissociated from CH_3I as I^- and subsequently neutralized.

The data of Fig. 1 and 2 indicate that whatever the process by which energy absorbed in the pentane is able to produce methyl radicals from added methyl iodide, the yield is not increased by concentrations of the additive greater than about 0.75 mole %. Thus if the dissociation is caused by electron capture or by a combination of electron capture and hydrogen atom attack all of the electrons or electrons and hydrogen atoms must be used up by CH_3I rather than by competing processes at concentrations above 0.75 mole %.

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(15) A. F. Trotman-Dickenson, J. R. Birchard and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 163 (1951).

(16) K. J. Ivin and E. R. Steacie, *Proc. Roy. Soc. (London)*, **A208**, 52 (1951).

(17) The value of 6.3 is obtained by first subtracting the 0.28 of line 6, column 3 of Table I from the 6.3 of line 4, column 3 of Table I which gives 6.0, the yield of thermal CH_3 from CH_3I, and then adding 0.3, which is the yield of $CH_4(C^{14})$ from $CH_3I(C^{14})$ in the presence of added I_2. This latter is the $G(CH_3(C^{14}))$ which is not affected by 0.25 mole % I_2 scavenger.

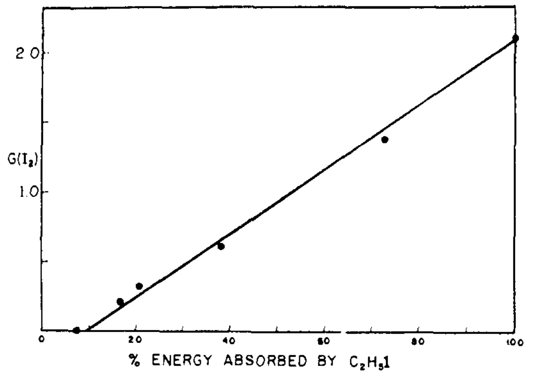

Fig. 3.—Yields of I_2 from the radiolysis of solutions of C_2H_5I in n-C_5H_{12}, as a function of concentration of C_2H_5I.

Line 10 of Table I shows the products observed when $C_2H_5I(I^{131})$ was irradiated in n-C_5H_{12} in the absence of I_2. A similar distribution, except for the parent radicals CH_3 and C_2H_5, was observed in two experiments with $CH_3I(I^{131})$ as the solute. The ten-fold higher G values for incorporation of I^{131} in pentyl iodides in these experiments than for incorporation of $C^{14}H_3$ labelled methyl in hexanes in the experiments of line 9 is attributable to the fact that the methyl radicals produced from CH_3I by electron attachment or hydrogen abstraction usually react with the solvent to form methane before encountering another radical, whereas the I atoms cannot react with the solvent and have no alternative but to react with radicals or the walls. It seems necessary to consider reaction with the walls as probable since the total observed G(I) as indicated by the I^{131} products in line 10 is only 1.2 as contrasted to the indication of a net G of 4.9 for formation of C^{14} labelled products from $CH_3I(C^{14})$ (line 9).

Iodine Production During the Radiolysis of Ethyl Iodide–Pentane Solutions.—Duplicate samples of ethyl iodide in pentane at each of five concentrations (4.8, 9.7, 12.5, 25.2 and 58.8 mole %) were irradiated at a dose rate of 5×10^{18} e.v. g.$^{-1}$ min.$^{-1}$ for 20 minutes. The iodine concentration as a function of dose was measured by absorption spectrometry. No absorption due to I_2 was observed in the irradiation of the 4.8% solution, indicating that $G(I_2)$ in such solutions is certainly less than 0.003 and may be zero. For the solutions containing 9.7 mole % and higher concentrations, iodine was produced continuously from the start of irradiation. In each case the initial $G(I_2)$ was somewhat lower than a constant value which was observed after the I_2 concentration exceeded a value of about 5×10^{-5} M.[18] The dose-independent $G(I_2)$ values observed after the induction period were 0.20, 0.32, 0.59 and 1.28 for the 9.7, 12.5, 25.2 and 58.8% solutions, respectively. These G values (calculated on the basis of total energy absorbed by the solution) are plotted in Fig. 3 as a function of the fraction of the energy absorbed by the solution which was absorbed directly by the C_2H_5I. The energy absorbed by the C_2H_5I is estimated from its electron % in the solution. For these solutions the calculation of the total energy absorbed included consideration of the disproportionate absorption of the gamma radiation by I atoms as a result of their high atomic number which increases absorption by the photoelectric effect. This has negligible effect on the fraction of total energy lost to C_2H_5I because most of the energy is transferred to the molecules by the Compton electrons rather than by the gamma rays.

G(radicals) in the radiolysis of pentane, as determined by I_2 scavenger studies in this work (Table I) and by the disappearance of I_2,[11] is about 8.2. $G(^1/_2\ I_2)$ in the radiolysis of pure ethyl iodide is 4.2.[19] Consequently, no iodine production would be expected in solutions of C_2H_5I in n-C_5H_{12} at C_2H_5I concentrations below that at which about twice as much energy is absorbed by C_2H_5I as by C_5H_{12}, unless the proximity of the two components in the same solution lessens the G of radical production from the pentane or increases the G of $^1/_2\ I_2$ from the ethyl iodide. Figure 3 shows that iodine is observed at concentrations where 90% of the energy is absorbed by the n-C_5H_{12}. Analogous results, showing I_2 production during the radiolysis of cyclohexane solutions containing 5 mole % CH_3I or C_2H_5I have been reported.[20]

As illustrated by comparison of lines 3–6 of Table I with line 2, low alkyl iodide concentrations reduce radical production from the hydrocarbon solvent. This reduction of about $(8.2 - (11.6 - 6)) = 2.6$ G units presumably accounts in part for the production of I_2 at low concentrations. It is accompanied by an added production of 6 G units of radicals from the alkyl iodide, but this cannot decrease the net I_2 yield since each of these radicals is formed in conjunction with the formation of either I^-, I or HI.

A similar reduction in radical production from heptane–iodine solutions is suggested by the observation[21] that the $G(-I_2)$ initial for the radiolysis of 0.02 mole % I_2 solutions which is 3.4 is changed to 2.5 for identical solutions containing 0.1 mole % C_2H_5I. In the same work[21] it was shown that $G(-I_2)$ decreases with accumulated dose and this was attributed to the accumulation of alkyl iodide products.

The nearly linear dependence of $G(I_2)$ on the fraction of the energy absorbed by C_2H_5I, shown in Fig. 3, over the range from about 10% to 100% is surprising. In pure ethyl iodide the thermal free radicals, produced with a G of 4.2, are consumed in competitive reactions with HI and I_2 while an additional 2.2 G units of carbon–iodine bond rupture results from reactions which are not sensitive to scavenger action. This latter type of reaction would be expected to be dependent on the type of neighboring molecules. As the concentra-

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[18] The most probable explanation of the short induction period seems to be the presence of a small amount of impurity, perhaps an alkene, in the Phillips' "Pure Grade" pentane which has a stated purity of "99% minimum."

[19] R. J. Hanrahan and J. E. Willard, *J. Am. Chem. Soc.*, **79**, 2434 (1957).

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[21] R. J. Hanrahan, Ph.D. Thesis, University of Wisconsin, 1957, available from University Microfilms, Ann Arbor, Michigan.

tion of ethyl iodide increases along the abscissa of Fig. 3, the energy absorbed directly by C_2H_5I, the ratio $G(HI)/G(I_2)$, the G of radicals formed from n-C_5H_{12}, and the nature of the chemical environment of each reactive species are presumably all changing. The net sum of these effects yields the straight line relationship.

Conclusions.—The work reported here seems to require that the reaction $RI + e^- \rightarrow R + I^-$ occurs to a significant extent to explain the yield of R radicals from RI additives during the radiolysis of RI–pentane solutions. Figures 1 and 2 indicate that the concentration range of RX in which the R radical yield rises from low values to its saturation value is similar to the range suggested by Platzman[4] as the most probable for the competition of solutes for subexcitation electrons which would otherwise undergo recombination with positive ions. If electron attachment plays a significant role it must be that in these solutions the immediate recapture of electrons by the parent positive ion suggested by the estimates of Samuel and Magee[22] does not occur with high probability, or that the probability of the $e^- + RI \rightarrow R + I^-$ reaction is sufficiently high (requiring of the order of 10 collisions or less) that it can compete for the electron while it is making its round trip from the positive ion into the solution and back. Escape of the electrons from the parent positive ion is suggested by experiments of R. Ahrens[23] and B. Suryanarayana in our laboratory, in which the change in electrical conductivity of liquid ammonia caused by exposure to 10^{18} e.v. g.$^{-1}$ min.$^{-1}$ of Co^{60} gamma radiation was measured. These are consistent with the conclusion that the steady state concentration of ion pairs caused by the radiation field was 4×10^{12} cc.$^{-1}$.

The evidence of this paper and earlier work both suggest that radical production from irradiated hydrocarbons is reduced when neutralization of RH^+ ions occurs by charge transfer from negative ions, such as I^-, rather than by combination with free electrons. If this is so it means that radical yields for hydrocarbons deduced from iodine scavenger studies may be lower than the actual radical yields in the pure hydrocarbons.

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[CONTRIBUTION FROM UNION CARBIDE EUROPEAN RESEARCH ASSOCIATES, S.A., BRUSSELS, AND UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN]

The Preparation, Properties and Structure of the Iron Carbonyl Carbide $Fe_5(CO)_{15}C$

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The reaction of $Fe_3(CO)_{12}$ with methylphenylacetylene and in particular with pentyne-1 gives besides organometallic complexes a small quantity (*i.e.*, less than 0.5% yield in the most favorable cases) of a new type of polynuclear metal complex of formula $Fe_5(CO)_{15}C$. The conditions of preparation and properties of $Fe_5(CO)_{15}C$ are described. Magnetic and infrared spectral studies show the solid to be diamagnetic with no bridging carbonyl groups. Its molecular configuration was found by a three-dimensional X-ray analysis to consist of an approximate equilateral tetragonal pyramid of iron atoms with three terminal carbonyls attached to each iron. A new structural feature is the presence of a penta-coördinated carbon atom located slightly below the center of the basal plane of iron atoms at approximately equal distances from each of the five iron atoms. This carbon atom with its four valence electrons allows each iron to attain a "closed shell" electronic structure in the ground state. A qualitative MO description of the new type of bonding is given.

Introduction

The reactions of the three iron carbonyls with alkynes in inert solvents[4-10] have produced a variety of organoiron carbonyl complexes with unusual structural features and novel types of bonding. The present paper reports the preparation and characterization by both chemical and physical means of a new type of compound, a polynuclear metal carbonyl carbide, of formula $Fe_5(CO)_{15}C$.

This compound was isolated in small amounts during the investigation of the reactions between alkynes and triiron dodecacarbonyl.[4-6] In particular, formation of $Fe_5(CO)_{15}C$ was observed on heating $Fe_3(CO)_{12}$ with methylphenylacetylene or pentyne-1 in petroleum ether. The compound could only be obtained in 0.5% yield in the most favorable cases, and all attempts to increase the yield were unsuccessful. Elemental chemical analysis indicated an approximate $Fe(CO)_3$ species. The degree of polymerization in the crystalline state was established by a three-dimensional X-ray study reported here which not only showed the molecular

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[3] National Science Foundation Predoctoral Research Fellow, 1959–1961. The X-ray work is abstracted in part from the Ph.D. Thesis of Dale L. Wampler, University of Wisconsin, January 1962.

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