

tion is the larger term, but whether it determines the above trend is not known. An attempt to measure the activation energy for the dissociation of $P(OC_4H_9)_3$ from *cis*- $Mn(CO)_3[P(OC_4H_9)_3]_2Br$ was made using the method employed for the $P(OC_6H_5)_3$ complex. Thus $P(C_6H_5)_3$ was added to a solution of *cis*- $Mn(CO)_3[P(OC_4H_9)_3]_2Br$, but in this case no reaction occurred, and the isomerization proceeded as usual.

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The Mercury(3P_1)-Sensitized Photolysis of Some Liquid Alkanes at 25 $^{\circ}$

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The liquid phase mercury-photosensitized decompositions of *n*-hexane, *n*-pentane, isopentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane have been investigated. The mechanism of this liquid phase photolysis is similar to that of the low temperature vapor phase investigations. The photolysis products are hydrogen, parent olefin, and parent dimer with no carbon-carbon cracking products. One primary process associated with the quenching of $Hg(^3P_1)$ atoms is the formation of a mercury complex. This complex and product olefins alter the "effective" mercury concentration while trace impurities completely remove a large fraction of it. Quantum yields for hydrogen production are all nearly one, indicating complete quenching of excited mercury atoms. Olefin products have a quantum yield of about 0.4 for hydrocarbons containing only secondary and primary H-atoms. The presence of tertiary H-atoms increases the olefin yield considerably. This increase is reflected in the k_{dis}/k_{comb} which is less than 1 for secondary and primary radicals and greater than 2.5 for tertiary radicals. The precursors for dimer products are tertiary, secondary, and primary radicals. Tertiary-tertiary dimers are most important, but primary radical combinations become significant as the ratio of primary H atoms to secondary and tertiary H-atoms increases.

I. Introduction

Information regarding the reactions of large alkyl radicals in the liquid phase is meager. Production of these radicals by radiolysis and by chemical means usually is accompanied by the simultaneous production of a variety of products which obscure the radical reactions. A study of the liquid phase mercury-photosensitization of *n*-decane² indicated that the sole precursors of the final products were parent alkyl radicals and H-atoms. This technique thus should be suited for unambiguous study of alkyl radicals in the liquid phase.

In order for mercury-photosensitization to be a practical tool for the study of liquid phase decompositions, it is necessary that mercury be sufficiently soluble in the solvent to absorb significant quantities of incident light during a reasonable period of irradiation. Some solutions of mercury in hydrocarbons have been shown^{2,3} to extinguish much of the 2537-Å. mercury resonance radiation. Solubilities of mercury in various hydrocarbons⁴ all lie in the micromolar concentration range and vary only slightly from one hydrocarbon solvent to another. Absorption spectra of mercury in the hydrocarbons used for this investigation were found to be similar to one another and to exhibit the pressure broadenings and Stark effect splittings observed previously.^{2,3} These hydrocarbon-mercury solutions all absorb approximately 4% of the incident 2537-Å. radiation for each centimeter of path length.

Phibbs and Darwent² did not observe any C-C "atomic" cracking products or olefin products in the liquid phase mercury-photosensitized decomposition of *n*-decane, while similar vapor phase decompositions show that both types of products are important. The absence of liquid phase C-C "atomic" cracking products is in agreement with the low temperature vapor phase investigations of Taylor and Bates⁵ and Back,⁶ and

may be explained in terms of solvent stabilization effects, but the absence of olefin products in the *n*-decane system is surprising.

This investigation was initiated in an effort to evaluate the applicability of mercury-photosensitized decompositions to the liquid phase and to clarify the reaction mechanism by careful product analysis on a number of saturated hydrocarbon systems. Because additional information concerning the photosensitization process is needed, a third important facet of this investigation was an attempt to elucidate this mechanism.

II. Experimental

The light source used in these experiments was an Sc2537 low pressure mercury vapor lamp manufactured by the Hanovia Manufacturing Co. It is constructed of a Vycor envelope shaped into a four-coil spiral, a geometry identical with those lamps described in an earlier research from this Laboratory.⁷ Its output is 95% at 2537 Å. with small intensities at longer wave lengths.

Three reaction vessels were employed. All rate studies were carried out in a vessel consisting of a Vycor tube closed at one end and surrounded by a Vycor water jacket. The inner tube was connected to a Pyrex-Vycor graded seal to facilitate manipulation. A small side arm was attached to the vessel above the graded seal so mercury might be isolated from the system during filling and photolysis. The reaction volume of this vessel was 6.7 cc. Experiments requiring optical density measurements were performed in a vessel having similar construction, but with a reaction volume of 60 cc. and a 100-mm. quartz absorption cell fused to the vessel below the graded seal. A few experiments which involved high conversions were made in a 200-cc. Vycor vessel without a water jacket. This cell was attached to a 300-cc. ballast vessel to prevent the build-up of product pressure. Lamp intensity was measured by the uranyl oxalate actinometer using the modification of Pitts, *et al.*⁸ A number of measurements at several optical densities indicated a linear variation of absorbed intensity with optical density in the cylindrical vessels at the low optical densities possible in these experiments. Maximum output of the lamp was reached in 2 min., and corrections for this build-up time were negligible compared to photolysis times. For quantum yield determinations, it was necessary to take a time average of the absorbed intensity by measurement of the variation in optical density of the mercury-hydrocarbon system.

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(8) J. N. Pitts, Jr., J. D. Margerum, R. P. Taylor and W. Brum, *ibid.*, **77**, 5499 (1955).

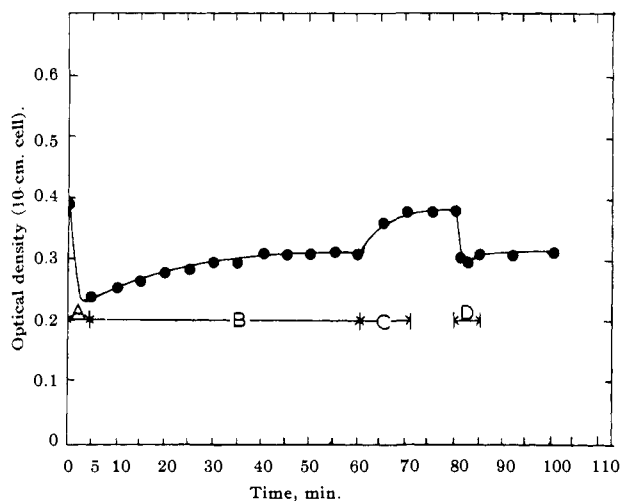


Fig. 1.—Variation of optical density with photolysis time for the mercury-*n*-hexane system. A, initial decrease in mercury concentration; B, attainment of a photostationary state; C, lamp off; D, photolysis resumed; $\tau = 2560 \text{ \AA}$.

All hydrocarbons were Phillips "Pure Grade." All were found to absorb an appreciable fraction of the incident light at 2537 \AA . Optical purity was obtained by passing the hydrocarbons through silica gel which had been heated previously to 200° for 24 hr. and cooled under vacuum. Hydrocarbons purified in this manner were degassed by the method of Newton⁹ and stored in evacuated ampoules prior to use. The mercury used as the solute was Fisher "Instrument Grade."

Prior to fusing the reaction vessel onto a vacuum sub-line, excess liquid mercury was injected into the side arm of the vessel *via* a syringe. The sub-line manifold was connected to an ampoule of degassed hydrocarbon, an empty storage ampoule, and a Dry Ice condenser for removal of water from the hydrocarbon. After evacuating at 10^{-3} mm. for 2 hr., mercury was frozen in the side arm and the sub-line isolated from the vacuum system. The storage ampoule was opened and hydrocarbon vapors condensed first on the Dry Ice condenser and then into the reaction vessel which was also held at -81° . After filling, all sources of hydrocarbon were frozen and the reaction vessel was sealed off under vacuum.

Mercury was dissolved into the solvent by agitation. Optical density measurements indicated a saturation time of 20 min. for continuous shaking at a temperature slightly higher than the saturation temperature. The small vapor phase zone above the liquid was darkened by opaque tape to minimize contributions from vapor phase photolysis. The system was allowed to attain thermal equilibrium at $25 \pm 0.2^\circ$ for 1 hr. by circulating distilled water from a constant temperature bath through the water jacket of the reaction vessel.

Photolysis periods ranged from 1–30 hr. In some experiments requiring optical density measurements at short intervals, room temperature was maintained at 25° to eliminate temperature effects on mercury concentration during these measurements. Optical measurements were made with a Beckman DU spectrophotometer modified to accept the 100-mm. cell which was sealed on the reaction vessel.

Gaseous products were removed from the solvent by bulb-to-bulb distillation and transferred to a pressure-volume apparatus with a Toeppler pump. After *PV* measurements, the entire sample was collected in a bulb and subjected to mass spectrometric analyses. Saturated liquid hydrocarbon products were analyzed, using a gas chromatograph equipped with a thermal conductivity detector and an 8-ft. \times 0.25-in. column packed with 15% Apiezon on 60–80 mesh Celite. Some qualitative standards for these products were prepared by standard organic techniques from Fisher "Practical" reagents. Olefin products were brominated using a solution of Br_2 in acetic acid. The excess Br_2 was treated with KI, followed by titration with $\text{S}_2\text{O}_3^{2-}$. With this procedure, standard olefin solutions of the same concentrations encountered in reaction products could be determined to $\pm 5\%$.

III. Results

Effect of Impurities on the Hydrocarbon System.—Accurate measurements of quantum yields in the Hg^3P_1 -sensitized photolysis of hydrocarbons demand an exact knowledge of the variation of mercury concentration with photolysis time. In a number of experi-

(9) A. S. Newton, *Anal. Chem.*, **26**, 1214 (1956).

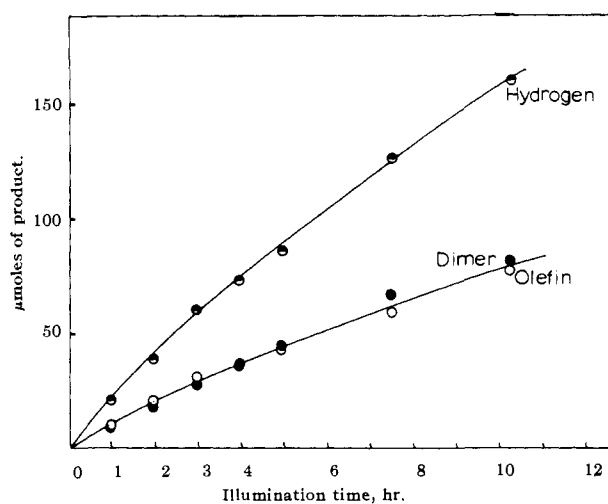


Fig. 2.—Product yield in the Hg^3P_1 -sensitized photolysis of *n*-hexane: \bullet , H_2 ; \circ , hexenes; \bullet , dodecanes (Ca).

ments, the optical density of each mercury-hydrocarbon system was measured at 5-min. intervals during the photolysis period. The *n*-hexane-mercury system, which is typical of all systems investigated, gave the optical density variation illustrated in Fig. 1. Region A corresponds to a rapid decrease in the mercury concentration to some minimum value at the initiation of photolysis. As the photolysis proceeds, mercury concentration gradually increases until a photostationary state is reached in region B. Photolysis was stopped at the beginning of region C. This resulted in a rapid rise in mercury concentration until the original saturation value was attained. If photolysis is resumed (region D), the mercury concentration drops immediately to its photostationary state and remains at that value for the duration of the photolysis. The initial drop was found to be due to mercury-removing impurities in the hydrocarbon system. When the saturated concentration was established after the initial drop, mercury concentration remained at the photostationary level during photolysis and regained the saturation concentration when photolysis was ceased.

Decomposition Products.—The detectable products of mercury-photosensitized decompositions in the liquid phase are hydrogen, parent olefin, and parent dimer. Quantum yields of these products for several alkanes are summarized in Table I. Product yields as a function of photolysis time for the *n*-hexane photodecomposition are shown in Fig. 2. In both Table I and Fig. 2, dimer yields are calculated from the difference in hydrogen and olefin yields. The validity of this calculation will be discussed later.

TABLE I
QUANTUM YIELDS FOR MERCURY-PHOTOSENSITIZED DECOMPOSITION OF SOME LIQUID ALKANES AT 25°

Alkane	$\phi \text{ H}_2$	ϕ (olefin)	ϕ (dimer)
<i>n</i> -Hexane	1.07 ± 0.04	0.54	0.53
<i>n</i> -Pentane	1.1	.4	.7
2,2-Dimethylbutane	1.11	.31	.80
Isopentane	1.30	.94	.36
3-Methylpentane	1.1 ± 0.2	.9	.2
2,3-Dimethylbutane	1.32	1.29	.03

Analyses of olefin products from the *n*-hexane photolysis are shown in Table II. Only small quantities of product olefin were present, but the analytical procedure is sufficiently accurate to be of quantitative value.¹⁰

(10) Analyses were performed by Gulf Research and Development Co. and have been described by T. J. Hardwick, *J. Phys. Chem.*, **64**, 1623 (1960).

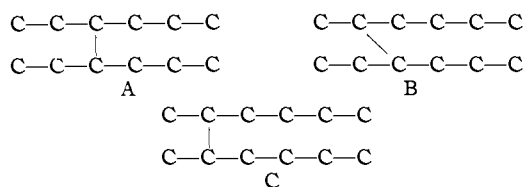
TABLE II
OLEFIN PRODUCTS OF THE MERCURY-SENSITIZED PHOTOLYSIS OF
n-HEXANE AT 25°

Olefin	0.5% Decomposition ^a	0.1% Decomposition ^b
Hexene-1	22.5%	34.8%
<i>trans</i> -Hexene (2 or 3)	4.6%	1.2%
<i>cis</i> -Hexene (2 or 3)	72.2%	56.0%
2-Methylpentene-2	...	1.2%
Unknown	...	6.6%

^a Solvent-olefin fraction separated from mercury-dimer fraction prior to analysis. ^b Entire sample subjected to analysis.

Considerable effort was expended in the analysis of dimer products for the *n*-hexane-mercury system for which no standards were available. A gas chromatogram of the dimers yielded three peaks in the ratios 1:2:1 in area. Extrapolation of peak areas of known quantities of *n*-dodecane at different retention times indicates the dimer yield for the *n*-hexane photolysis is equal to the difference in hydrogen and olefin yields. This mass balance is presumed to be valid for the other systems investigated.

Relatively large samples of the dodecane photolysis products from the *n*-hexane-mercury study were collected from the effluent of the chromatographic detector and subjected to n.m.r. and mass spectrometric analysis. A synthetic mixture prepared by the Wurtz reaction of a mixture of 2- and 3-bromohexane gave a chromatogram of three peaks with retention times identical with those of the dodecane products. These measurements indicated the three detectable products were the dodecanes A, B, and C, respectively, resulting from the statistical combination of 2- and 3-hexyl radicals. One determination of the dimer



fraction on a gas chromatograph equipped with a hydrogen flame detector revealed several products which were not seen on the T-C detector. These products constitute about 5% of the total dimer yield and are presumed to be combination products of parent radicals and radicals from the hydrocarbon impurities (<1%).

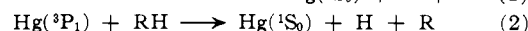
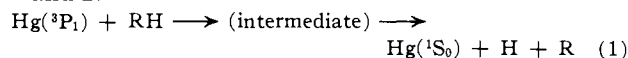
The dimer fractions for the Hg-sensitized photolysis of *n*-pentane, isopentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane also were analyzed using gas chromatography. In the case of *n*-pentane only two dimer peaks were observed, whereas five were found for isopentane. The gas chromatograms of 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane yielded four, five, and three dimer peaks, respectively. Standards are not available for the identification of these products, and it is dangerous to predict retention times of possible candidates without boiling point data. Nevertheless, the qualitative implications of these chromatograms are important.

IV. Discussion

An elementary calculation involving the intensity of absorbed light and the mercury concentration in a saturated hydrocarbon solution indicates that each mercury atom is used at least once for every 10 sec. of photolysis time. Therefore, slight traces of impurity would have a profound effect on the rate of product formation if this impurity completely removes mercury atoms from solution. The concentration of mercury-removing impurity, which can be estimated from the

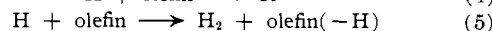
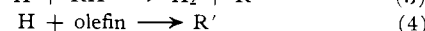
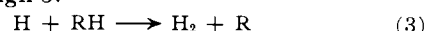
difference in mercury concentration between its minimum in region A and the photostationary state in Fig. 1, is approximately 10⁻⁴ mole %. This level of impurity is difficult to detect or remove and deviates very little from hydrocarbon to hydrocarbon. The trace impurity should not affect the distribution of photolysis products, a point supported by the consistency of data in Fig. 2.

Consideration of the photostationary state in Fig. 1 indicates the primary process in Hg(³P₁)-sensitized decompositions in the liquid phase may involve the formation of an intermediate which contains mercury. Rapid attainment of the photostationary state and the absence of any permanent mercury-containing products even for high decomposition experiments indicate the intermediate is not a result of excited mercury-photolysis product interactions, but a part of the primary process. The identity of this intermediate and its contribution to the primary process cannot be evaluated from this work. A promising candidate for this intermediate would be HgH formed by H-atom abstraction by an excited mercury atom. This species is short-lived in the gas phase, but the solvent may contribute to its stability. If HgH is the intermediate, it seems probable that the primary process is a combination of reactions 1 and 2.

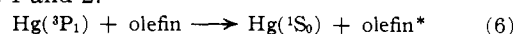


It is possible to rule out reaction 1 as the *exclusive* primary act on kinetic grounds. The intermediate decay follows a first-order kinetic equation and the lifetime (estimated from several observations in region C of Fig. 1) is about 400 sec. This lifetime is much too long to lead to the low steady state concentration of the intermediate observed in Fig. 1. If we postulate that only a small fraction of the primary process occurs *via* reaction 1, the long lifetime of the intermediate and its low steady state concentration may be reconciled. Thus, if reactions 1 and 2 are assumed to be the sole primary processes, reaction 2 must be some 2000 times more probable than reaction 1. If the lifetime of the mercury intermediate is shorter in the gas phase, as is reasonable, the failure to find kinetic evidence for it in earlier studies is readily understood.

Because the quantum yields for hydrogen production are consistently high, combinations of H-atoms with radicals or other H-atoms cannot be an important process. The fate of H-atoms may be summarized by reactions 3 through 5.



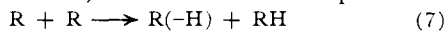
The decrease in the rate of hydrogen production with illumination time (Figure 2) might be attributed to scavenging of H-atoms by product olefin molecules (reaction 4), but this would not cause a decrease in radical concentration and cannot explain the observed decrease in the dimer yield. Furthermore, a series of experiments (not reported in detail here), in which olefins were added to scavenge H-atoms, yielded a negative value for k_5/k_4 when the data were treated in a manner analogous to that of Hardwick.¹⁰ These observations indicate that olefins interfere with the primary processes, probably by quenching the excited mercury atom (reaction 6) and lowering the rates of reactions 1 and 2.



It should be noted that the quantum yields for hydrogen (Table I) are consistently higher than one. These values are not energetically possible at 2537 Å.

for the hydrocarbons studied. Therefore, it is probable that a reproducible error in averaging mercury concentrations over the photolysis period resulted in the high quantum yields reported in Table I. Thus, while the relative quantum yields are reliable, the absolute value must be regarded with suspicion. It appears certain, however, that molecules possessing tertiary H-atoms give a greater hydrogen yield than those involving primary and secondary atoms only.

Darwent¹¹ measured the frequency of C-H bond rupture for primary, secondary, and tertiary C-H bonds by Hg(³P₁) to be 1:100:600, respectively. These approximate ratios have been confirmed recently by Holroyd and Klein.¹² This preference for rupturing tertiary and secondary C-H bonds is reflected in the hydrogen quantum yields and the dimer product distributions. Olefin and dimer products are formed by the disproportionation and combination of alkyl radicals (reactions 7 and 8). These radicals are products of



the primary interaction of Hg(³P₁) with parent molecules and H-atom abstractions from parent molecules. Isomerization of the 1-hexyl radical was shown to be negligible by analysis of the dimers in the photolysis of mercury di-*n*-hexyl¹³ and, apparently, does not compete with other radical reactions.¹⁴ Inasmuch as the intramolecular H-atom abstraction would appear to be more favorable for primary radicals than for secondary or tertiary radicals, it seems reasonable to conclude that isomerization does not alter significantly the identity of alkyl radicals in these experiments. Activation energies for H-atom abstractions from the parent molecule favor the production of tertiary, secondary, and primary radicals in approximately the ratios of 33:7:1,¹⁵ assuming equal frequency factors.

Dimer products of the *n*-hexane decomposition are the result of secondary-secondary radical combinations with primary radicals making an undetectable contribution. In molecules such as isopentane and 3-methylpentane, secondary and tertiary radicals are the predominant precursors to dimers, but the presence of primary radicals can be deduced from the number of dimer products appearing in their gas chromatograms. In the two special cases of 2,2-dimethylbutane (only primary and secondary C-H bonds) and 2,3-dimethylbutane (only primary and tertiary C-H bonds), the importance of primary C-H bond rupture is also indicated by the contribution of primary radicals to the dimer product. Even with quantitative analysis of these dimers, it would not be possible to predict the contribution of any single radical to the total photolysis because of unequal tendencies for primary, secondary, and tertiary radicals to disproportionate.

Ratios of olefin/dimer for the six hydrocarbons investigated are reported in Table III. These ratios involve the reactions of mixtures of radicals and, therefore, cannot be used to evaluate kinetic rate constants quantitatively. In spite of this, it is worthwhile to consider the olefin/dimer ratio as a qualitative measure of the average disproportionation to combination ratio for the radical mixture. These ratios for *n*-pentane and *n*-hexane are representative of k_7/k_8 for secondary radicals and, as expected, are quite a bit higher than the 0.15 value for 1-hexyl radicals in CCl₄.¹⁴ An independent determination¹³ of k_7/k_8 for 1-hexyl radicals in *n*-hexane by photolysis of mercury di-*n*-hexyl also

TABLE III
OLEFIN/DIMER RATIOS IN THE MERCURY-SENSITIZED PHOTOLYSIS OF SOME LIQUID ALKANES AT 25°

Alkane	Olefin/dimer
<i>n</i> -Pentane	0.67
<i>n</i> -Hexane	1.0
2,2-Dimethylbutane	0.39
Isopentane	2.6
3-Methylpentane	4.9
2,3-Dimethylbutane	42

indicates a low value of 0.33. Hardwick¹⁰ reported k_7/k_8 for hexyl radicals presumed formed in liquid hexane radiolysis to be 1.78–2.26. This value is twice as high as the values of 0.67 and 1.0 obtained here for *sec*-C₆H₁₁ and *sec*-C₆H₁₃ radicals, respectively. Therefore, it is difficult to reconcile the high olefin/dimer ratio obtained in hexane radiolysis with the values reported in Table III. It is possible that olefins may be formed in radiolysis by reactions of nonradical species, but speculation on this point is unwarranted here.

It is noteworthy that while secondary radicals may be the predominant product of 2,2-dimethylbutane photolysis, the disproportionation reaction is hindered by the structure of the molecule and the observed ratio is lower than that found for other secondary radicals. Tertiary radicals, which are expected to be the predominant species produced in the decomposition of isopentane, 3-methylpentane, and 2,3-dimethylbutane, show a higher tendency to disproportionate than to combine. It is interesting to note the relationship between the olefin/dimer ratio and the nature of the H-atoms adjacent to the most probable radical. *t*-Isopentyl radicals have both primary and secondary H-atoms available for abstraction, and its ratio is only half that of *t*-3-methylpentane radicals in which the number of *sec*-H-atoms which are candidates for abstraction is doubled. If an adjacent *t*-H-atom is present, as in 2,3-dimethylbutane, the ratio is many times higher, indicating a significant difference in the rate constants for these disproportionations at 25°.

V. Summary

Liquid phase mercury photosensitization is a relatively new method of studying molecular fragments in the liquid phase. Trace impurities have a profound effect on mercury concentration during photolysis, and added olefinic solutes quench excited mercury to the ground state. Therefore, the limitations of this method are severe.

The mechanism of the liquid phase mercury-sensitized photolysis is analogous to low temperature vapor phase investigations. The primary process involves an intermediate of the mercury atom with some fragment of the hydrocarbon molecule. This intermediate may or may not be important in the vapor phase. The ultimate products of the primary reaction are H-atoms and alkyl radicals. These radicals occur in the order: tertiary > secondary > primary. The importance of each type of radicals is reflected in the dimer distributions and the disproportionation/recombination ratios.

Acknowledgments.—This work was supported by the American Chemical Society Petroleum Research Fund, for which grateful acknowledgment is made. Special thanks are due to Dr. T. J. Hardwick (Gulf Research and Development Company) for calling the early study of Darwent and Phibbs to our attention and for arranging the hexene analyses. The authors also wish to thank Dr. B. J. Mair for separation of the dodecanes, Dr. R. J. Kurland for interpretation of the n.m.r. spectra, and Mr. S. Wrbican for operation of the mass spectrometer.

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(13) R. Kuntz and G. J. Mains, unpublished data.

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