dium triphenylmethyl in ether have been measured.

2. A value for the ionization constant of this compound is found and the methods of estimating it are discussed.

3. The effect of this value on the value of the electron affinity of triphenylmethyl is calculated. The revised value is −48 ± 5 kcal.

CAMBRIDGE, MASS. RECEIVED APRIL 6, 1938

[CONTRIBUTION FROM THE RESEARCH LABORATORIES DIVISION, GENERAL MOTORS CORPORATION]

The Induced Liquid Phase Decomposition of Hydrocarbons

BY PAUL L. CRAMER

The induced decomposition of hydrocarbons by means of known free radical producing compounds has been studied by a number of investigators. These reactions with various hydrocarbons, carried out in both the vapor and liquid phase, have been initiated by the thermal and photochemical decomposition of small amounts of metal alkyls and aryls, azo compounds, ethylene oxide, aldehydes, ethers, and ketones. The vapor phase induced decomposition of *n*-butane[1] gave the normal thermal reaction products. Similar results have been obtained with *n*-pentane at high reaction pressures.[2] The induced decomposition of other gaseous paraffins has been reported.[3] The report by Echols and Pease that ethane is inert when compared with propane and butane in such induced reactions is in accord with certain data presented in this paper. Similar gaseous phase reactions with the olefins have been reported only for ethylene.[4] The induced ethylene reaction in benzene solution has been described.[5] Other induced liquid phase reactions of hydrocarbons are included in a recent literature review.[6]

In a previous paper[5] the author reported on the thermal decomposition of relatively large amounts of tetraethyllead in solution in various types of hydrocarbons; however, only the results for benzene and for benzene in the presence of ethylene and hydrogen were described in detail. The purpose of the present paper is to describe the liquid phase decomposition of relatively large amounts of tetraethyllead in a number of liquid paraffinic, olefinic, aromatic, and hydroaromatic hydrocarbons. The hydrocarbons used in these experiments were *n*-heptane, 2,2,3-trimethylbutane, 2,2,4-trimethylpentane, *n*-decane, cyclohexane, 1-hexene, 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene, 3,3-dimethyl-1-butene, 1-heptene, 2,3,3-trimethyl-1-butene, diisobutylene, cyclohexene, benzene, naphthalene, tetrahydronaphthalene, and decahydronaphthalene. These experiments were carried out in a bomb at reaction temperatures of 200 to 300°. The course of the reaction was followed by a complete analysis of the gaseous reaction products, and in certain cases the oily liquid reaction products were examined.

Contrary to a recent statement in the literature[6] that "no solvent has yet been discovered which is inert to free radicals," the aromatic hydrocarbons, benzene and naphthalene, appear to be quite inert to the decomposition products of tetraethyllead at temperatures below 300°. Induced reactions were obtained with all of the paraffins, olefins, and hydroaromatics included in this study. The apparent type and extent of the reactions appear to be determined largely by the class and the molecular structure of the hydrocarbon.

In contrast to the vapor phase reactions, the conversion products formed in the liquid phase consist entirely of high boiling hydrocarbons. This fact is a great aid in determining the probable course of the decomposition products of tetraethyllead free from the interference of any gaseous reaction products of the hydrocarbon itself. For the comparison of the results obtained with different hydrocarbons, the liquid phase method has certain disadvantages. Due to the differences in vapor pressure, the concentration of tetraethyllead varies appreciably with various hydrocarbons. Although the reaction temperatures are comparable for any class of hydrocarbons, it varies considerably with different classes.

As previously proposed,[5] the liquid phase reactions may best be explained by assuming that

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[1] Frey, *Ind. Eng. Chem.*, **26**, 200 (1934).

[2] Unpublished data from this Laboratory.

[3] Heckert and Mack, THIS JOURNAL, **51**, 2706 (1929); Echols and Pease, *ibid.*, **58**, 1317 (1936).

[4] Taylor and Jones, *ibid.*, **52**, 1111 (1930); Rice and Sickman, *ibid.*, **57**, 1384 (1935).

[5] Cramer, *ibid.*, **56**, 1234 (1934).

[6] Hey and Waters, *Chem. Rev.*, **21**, 169 (1937).

the reactions are induced by free ethyl radicals according to equations (1) and (2), which have been proposed as

$$C_2H_5— + R—H \longrightarrow R— + C_2H_6 \qquad (1)$$
$$C_2H_5— + RCH{=}CH_2 \longrightarrow RCH(C_2H_5)CH_2— \qquad (2)$$

the primary reactions of free radicals with paraffins[7] and olefins.[4] Reaction (1) may apply to all classes of hydrocarbons. In the case of metal alkyls, the possibility of "nascent" metals acting as inducers in these reactions has been considered.[8] In this connection it may be of interest to mention that attempts to induce reactions in both paraffins and olefins by the thermal decomposition products of iron and nickel carbonyls under comparable conditions of temperature and pressure gave negative results.[2]

Since reaction (1) involves only the hydrogen in the molecule, the importance of the relative reactivities of the different kinds of hydrogen atoms in the hydrocarbon molecule is given greater consideration in the discussion of the present data than previously considered for the thermal reactions of hydrocarbons.[9] Likewise, the effects of both the kind of hydrogen and the position of the double bond in the olefin molecule on both reactions (1) and (2) are discussed.

Since reaction (1) is a fundamental reaction type proposed in the chain reaction mechanisms for both the pyrolysis[7] and the oxidation[10] of hydrocarbons, certain analogies of the present reaction data with certain data on the stability, the oxidation, and the knocking characteristics of hydrocarbons are pointed out.

Experimental

Materials.—2,2,4-Trimethylpentane, *n*-decane, cyclohexane, cyclohexene, diisobutylene, benzene, naphthalene, tetrahydronaphthalene, and decahydronaphthalene were obtained from commercial sources, and were dried and purified by fractionation. The remaining hydrocarbons, chiefly olefins, were synthesized in this Laboratory by the usual methods.

Commercial tetraethyllead was purified by the previously described procedure.[5]

Apparatus and Procedure.—The apparatus and the detailed procedure for the decomposition of tetraethyllead in benzene have been described.[5] Essentially the same procedure was used in the present experiments.

Since the present procedure does not permit comparable mole concentrations, the volume concentration of tetraethyllead was considered from the standpoint of providing sufficient solvent to dissipate the heat of reaction. Thus, in all of the experiments 50 cc. of the solvent hydrocarbon was used with varying concentrations of tetraethyllead (9.75 and 19.5 cc.). The lower amount of tetraethyllead was considered as the minimum amount necessary to furnish sufficient reaction gas for accurate analyses, whereas the higher concentration was considered as the maximum amount from the standpoint of both reaction temperature and pressure.

The initial reaction temperature, as indicated by the rise in pressure, was approximately 200° for the paraffins and benzene. The initial reaction temperature for the olefins, naphthalene, and the hydroaromatics appeared to be 220 to 235°. With the exception of the olefins, the main part of the reaction extended over a temperature range of 20 to 30°. Due to the higher heats of reaction, the main reaction with the olefins extended over a temperature range of 50 to 80°. Thus, in the case of the olefins, the final reaction temperatures approached or exceeded the critical temperature of the hydrocarbon; however, as indicated by the normal type of gaseous reaction products, and particularly by the absence of methane in the gas, it is believed that most of the reaction took place in the liquid phase. To ensure the complete decomposition of the tetraethyllead, the reaction mixture was finally kept at a temperature of 260–265° for three to four hours.

Due to the differences in the vapor pressure of the solvent hydrocarbons, and also the great variation in the amounts of the gaseous reaction products, the reaction pressures varied over a great range. In most of the experiments the reaction pressures varied between 20 and 50 atmospheres. In a few instances the pressure approached 100 atmospheres.

The comparatively simple gaseous reaction mixture, which consisted mainly of paraffins, was analyzed by means of a standard Burrell apparatus. The results thus obtained were confirmed by the fractionation of representative runs by means of a Podbielniak apparatus, supplemented by the regular absorption and combustion methods. In those experiments in which the amount of sulfuric acid soluble olefins was in excess of 100 cc., a fractionation of this fraction showed that it consisted of a mixture of propylene and butylene.

The liquid reaction products, light colored oils, were separated from the solvent hydrocarbons by fractionation in a small efficient spiral column. Tests were made in all the liquid products for unchanged tetraethyllead by adding bromine to the liquid sample dissolved in a small amount of absolute ether. In certain cases the liquid product was examined for its paraffin content by washing with sulfuric acid. In the experiments with the hydroaromatics, the reaction products were examined for their possible naphthalene content by sublimation tests.

The lead residues were examined for carbon by dissolving the lead in nitric acid.

Results and Discussion

An outline of the experiments together with the analytical and certain theoretical data are presented in Table I.

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[7] Rice, THIS JOURNAL, **53**, 1959 (1931); **55**, 3035 (1933).

[8] Burk, Thompson, Weith and Williams, "Polymerization," Reinhold Publishing Corp., New York, N. Y., 1937, p. 130.

[9] F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, Md., 1935, pp. 75, 100.

[10] For complete references see Elbe and Lewis, *Ind. Eng. Chem.*, **29**, 551 (1937); THIS JOURNAL, **59**, 976 (1937).

In calculating the percentage conversion of ethyl radicals to ethane, Table I, it is assumed that the hydrogen, butane, and ethane are, in addition to reaction (1), the products of reactions (3), (4), and (5).

$$2C_2H_5 \longrightarrow H_2 + 2C_2H_4 \quad (3)$$
$$2C_2H_5 \longrightarrow C_2H_4 + C_2H_6 \quad (4)$$
$$2C_2H_5 \longrightarrow C_4H_{10} \quad (5)$$

The absence of methane and the simplicity of the gaseous reaction products favors the above assumption. Further evidence is provided in the experiments with cyclohexene and tetrahydronaphthalene, in which ethane is the only paraffin present in the gaseous products. Therefore, in calculating the percentage conversion of ethyl radicals to ethane, the amount of introduced ethyl radicals is corrected for those consumed in reactions (3) and (5) as calculated from the amounts of hydrogen and butane found in the reaction gas.

As shown by the data in Table I, there is a great difference in both the type and extent of the reactions with various hydrocarbons as indicated by the percentage conversion of the hydrocarbons, and also by the percentage conversion of ethyl radicals to ethane.

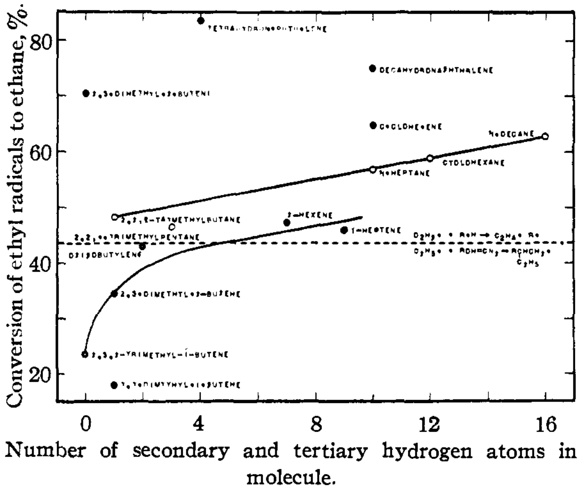

Fig. 1.—Relationship of molecular structure to assumed reactions of ethyl radicals with hydrocarbons: data from Table I.

There is no detectable amount of reaction with benzene and naphthalene and, as indicated by the amount of ethane formed in both hydrocarbons, it appears that the predominating reaction of the ethyl radicals was that of disproportionation, reaction (4), and also that the ethylene so formed was converted to liquid products presumably by reaction (1).

With both the paraffins and hydroaromatics the extent of the reactions is roughly proportional to the percentage of ethyl radicals converted to ethane. This evidence supports the assumption that the reactions were initiated by reaction (1). Further evidence for reaction (1) is the fact that no detectable amount of naphthalene was formed in the reactions with the hydroaromatic hydrocarbons, which would be expected in the case of dehydrogenation and the subsequent hydrogenation of ethylene to ethane.

There is a high percentage conversion of all olefins to higher boiling products; however, there is no simple relationship between the extent of the reactions and the percentage of ethyl radicals converted to ethane. The experimental evidence favors the assumption that the conversion of the olefins is induced by two different types of reactions: namely, by reaction (2), in which the ethyl radicals are consumed in the reaction, and by reaction (1), in which the ethyl radicals are converted to ethane. Further evidence for reaction (2) with the highly branched alpha olefins, 3,3-dimethyl-1-butene and 2,3,3-trimethyl-1-butene, is the unusually high percentage (40 and 60%) of paraffins found in the liquid reaction products, which is indicative of a high percentage of alkylation of the double bond.

The type and extent of the reactions with the active hydrocarbons appear to be associated not only with the class of hydrocarbon, but also, in the case of the open chain paraffins and olefins, the reactions appear to be associated with the molecular structure of the hydrocarbon. Since reaction (1) involves only the hydrogen in the hydrocarbon molecule, the relative amounts and reactivities of the primary, secondary, and tertiary hydrogen atoms in the molecule would be expected to determine largely the influence of molecular structure on this reaction with the paraffins. Likewise, the relative amounts of reactions (1) and (2) with the olefins, as influenced by the molecular structure, would involve the amount and kind of hydrogen atoms in the molecule, as well as the reactivity of the double bond. This relationship is shown in Fig. 1, in which the percentage conversion of ethyl radicals to ethane is plotted against the number of secondary and tertiary hydrogen atoms in the molecule.[11] The broken line at 43.5% conversion of ethyl radicals to ethane

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[11] The number of secondary and tertiary hydrogen atoms in the hydrocarbon molecule may be considered as a measure of the extent of branching or the chain length of the hydrocarbon.

TABLE I

DECOMPOSITION OF TETRAETHYLLEAD IN VARIOUS HYDROCARBONS[a]

Name	Tetraethyllead, cc.	Gaseous reaction products, cc. H_2SO_4 sol. olefins	C_2H_4	H_2	C_4H_{10}	C_2H_6	Conversion of hydrocarbons, %	Conversion of C_2H_5— to C_2H_6, %
n-Heptane	19.5	Nil	150	21	500	4509	21	56.9
n-Heptane	19.5	26	200	16	320	4688	20	56.6
2,2,3-Trimethylbutane	19.5	74	222	32	428	3874	2	48.2
2,2,4-Trimethylpentane	19.5	146	176	27	845	3366	3	46.6
2,2,4-Trimethylpentane	19.5	125	300	Nil	685	3510	2	46.2
n-Decane	19.5	70	245	47	318	5160	32	63.5
Cyclohexane	19.5	16	153	38	174	5069	11	59.4
Cyclohexane	19.5	22	228	27	215	4933	10	58.2
1-Hexene	9.75	259	214	72	62	1981	53	47.1
2,3-Dimethyl-1-butene	9.75	32	202	86	16	1478	50	34.5
2,3-Dimethyl-2-butene	9.75	Nil	168	39	59	3017	28	70.4
3,3-Dimethyl-1-butene	9.75	41	126	41	78	764	58	18.0
1-Heptene	19.5	229	342	81	455	3618	65	45.8
2,3,3-Trimethyl-1-butene	19.5	97	278	13	162	2000	48	23.2
2,3,3-Trimethyl-1-butene	19.5	117	286	13	177	2067	54	24.1
Diisobutylene	19.5	194	158	5	1670	2483	42	44.3
Diisobutylene	19.5	162	157	5	1620	2427	42	42.6
Cyclohexene	19.5	80	514	99	Nil	5507	32	62.9
Cyclohexene	19.5	110	460	155	Nil	5755	30	66.5
Benzene	19.5	16	120	56	114	3694	Nil	43.0
Benzene	19.5	41	115	41	234	3669	Nil	43.0
Naphthalene	19.5	26	236	120	157	3751	Nil	44.6
Naphthalene	19.5	30	238	74	155	3833	Nil	44.1
Tetrahydronaphthalene	19.5	Nil	286	85	Nil	7349	66	83.5
Tetrahydronaphthalene	19.5	Nil	394	80	Nil	7241	70	82.3
Tetrahydronaphthalene	9.75	83	257	99	Nil	3701	50	86.5
Decahydronaphthalene	19.5	28	347	104	195	6275	50	75.0
Decahydronaphthalene	19.5	21	396	69	272	6192	50	74.8

[a] Fifty cc. of the hydrocarbon used in all of the experiments.

represents the inert hydrocarbons, benzene and naphthalene. Reaction (1) may be considered as the predominating reaction with the hydrocarbons in the area above the broken line, whereas the reaction (2) may be considered as the predominating reaction with the hydrocarbons in the lower area.

As shown in Fig. 1, the apparent extent of reaction (1) with the paraffins is proportional to the number of secondary and tertiary hydrogen atoms in the molecule. These data indicate that the primary hydrogen in the paraffin molecule is comparatively unsusceptible to this type of reaction. It is interesting to note that cyclohexane, in which all the hydrogen is considered as secondary hydrogen, falls in line with the open chain paraffins.

Judging from the heats of hydrogenation of the substituted ethylenes,[12] the susceptibility of the double bond to reaction (2) would be expected to be somewhat the same for the alpha olefins. Therefore, as indicated by the percentage conversion of ethyl radicals to ethane, Fig. 1, the comparative non-susceptibility of the primary hydrogen in the alpha olefins to reaction (1) is more pronounced than for the same reaction with the paraffins. Reaction (1) appears to predominate over reaction (2) with the normal olefins, 1-hexene and 1-heptene. In contrast to the alpha olefins, 2,3-dimethyl-2-butene appears to be relatively unsusceptible to reaction (2). This is in accord with the comparatively low heat of hydrogenation for this hydrocarbon.[12] However, in contrast to the paraffins and the alpha olefins, the primary hydrogen in this hydrocarbon appears to be quite susceptible to reaction (1). Cyclohexene is apparently quite susceptible to reaction (1).

As would be expected from the previously known reactivity of the hydrogen atoms in the hydroaromatic hydrocarbons, tetrahydronaphthalene and decahydronaphthalene appear to be very susceptible to reaction (1).

The possible effect of experimental variables, particularly that of the concentration of tetra-

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[12] Conant and Kistiakowsky, *Chem. Rev.*, **20**, 181 (1937).

ethyllead, on the above data may be judged from those experiments in which the volume concentration of tetraethyllead varied in the ratio 2 to 1. In the case of tetrahydronaphthalene, a decrease of tetraethyllead from 19.5 to 9.75 cc. increased the percentage conversion of ethyl radicals to ethane by 4.2%, which is 11% of the difference in the conversion figures for benzene and tetrahydronaphthalene at the higher concentrations of tetraethyllead. Similarly, the wide difference in the concentration of tetraethyllead may possibly offer an explanation for the apparent inverse order of the conversion figures for 1-hexene and 1-heptene. In certain experiments in which the volume concentrations of tetraethyllead are the same at room temperatures, the differences in the mole concentrations are much smaller at the reaction temperature (200°), due to the increase in the vapor pressure with a decrease in the molecular weight. Thus, although the liquid phase experiments cannot be considered sufficiently comparable for hydrocarbons having small differences in molecular structure, it is believed that the above data furnish a relative reaction picture of both the type and extent of the reactions with various classes of hydrocarbons, and also with those hydrocarbons in any particular class which have reasonably wide differences in molecular structure.

If, as the above data indicate, there is a reasonably wide difference in the reactivity of the primary hydrogen as compared with the secondary and tertiary hydrogen in the hydrocarbon molecule at somewhat higher reaction temperatures, reaction (1) is a very important factor in determining the relative reactivity of hydrocarbons from the standpoint of the proposed chain mechanisms for the pyrolysis and the oxidation of hydrocarbons. From this standpoint the present data agree with certain theoretical and experimental data on the thermal reactions of hydrocarbons.

The above concept is in agreement with the free energy data on a limited number of paraffins.[13]

The oxidation of propane under moderate pressures[14] provides data concerning the possible effect of the kind of hydrogen in the molecule on reaction (1) in which, in addition to R—, RO—, or other radicals may be considered as carriers in the reaction chain. These data show that isopropyl and *n*-propyl alcohols are formed in a ratio as high as 5 to 1. This high isomeric ratio, favoring the iso derivative, is quite significant in view of the fact that from a probability standpoint the normal alcohol is favored by a ratio of 3 to 1.

Since it has been shown that knock in the internal combustion engine is associated with preflame reactions,[15] the degree of knock may be considered as a measure of the relative susceptibility of hydrocarbons to oxidation ahead of the normal flame front. Also, since the susceptibility of paraffins to knock has been shown to be proportional to the degree of decentralization of the molecule, and also to the length of the hydrocarbon chain,[16] the knocking characteristics of the paraffins may possibly be considered as a correlation of the susceptibility to oxidation with the number of secondary and tertiary hydrogens in the hydrocarbon molecule.

Summary

A study has been made of the induced liquid phase decomposition of a number of paraffinic, olefinic, aromatic, and hydroaromatic hydrocarbons as initiated by the thermal decomposition products of tetraethyllead.

With the exception of the aromatic hydrocarbons, induced reactions occurred with all of the hydrocarbons, the type and the extent of the reactions apparently depending on both the class and the molecular structure of the hydrocarbon.

Evidence has been presented in support of the assumptions that the induced reactions are initiated by free ethyl radicals, and also that the influence of the class and the molecular structure of the hydrocarbon on the reactions may be determined by the relative amounts and reactivities of the primary, secondary, and tertiary hydrogen atoms in the molecule.

Certain analogies between the reaction data and certain data on the stability, the oxidation, and the knocking characteristics of the paraffins from the standpoint of chain mechanisms involving free radicals have been pointed out.

DETROIT, MICH. RECEIVED APRIL 15, 1938

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[13] Rossini, *Ind. Eng. Chem.*, **29**, 1424 (1937).

[14] Newitt and Thornes, *J. Chem. Soc.*, 1665 (1937).

[15] For complete references see Withrow and Rassweiler, *Ind. Eng. Chem.*, **28**, 672 (1936); *J. Soc. Automotive Eng.*, **39**, 297 (1936).

[16] Lovell, Campbell and Boyd, *Ind. Eng. Chem.*, **23**, 26 (1931).