at virtually any experimental conditions. In turn, since dosimetry gives the rate of initiation and conversion data yield the rate of propagation, the radiation technique can give valuable insight into the nature of long chain reactions.

Our recent work has emphasized radiation-induced reactions between low molecular weight paraffins and olefins at rather high temperatures and pressures. Some observations made on the methane–ethylene reaction seem to warrant publication at this time although the work aimed at deciding whether this reaction is free radical or ionic in nature is still incomplete. The results are of definite interest regardless of which one of these alternative mechanisms is ultimately accepted.

Experimental.—Static experiments were made in electrically heated stainless steel systems having a surface/volume ratio of 1 cm.$^{-1}$. The radiation source consisted of a 3200 curie Co^{60} source,[4] and the dosimetry was done by Fe^{++}–Fe^{+++} conversion[5] with an uncertainty of ± 15%. Radiation and thermal experiments were made in identical reactors and at the same conditions using Phillips pure grade (>99.5%) methane and ethylene. Products were analyzed by gas–liquid partition chromatography to ±4% of the amount present. The experimental conditions were: 55 atm. total pressure, 10 mole per cent. initial C_2H_4 concentration, 343–426° temperature, and 0.12×10^6 rad./hr. (absorbed). The radiation yields are integral *G* values obtained directly from the radiation-induced reaction since at identical conditions no thermal reaction was observed.

Results and Discussion.—The homogeneous gas phase reaction between CH_4 and C_2H_4 is a notoriously slow process, presumably as a result of the slow unimolecular formation of $CH_3\cdot$ and $H\cdot$ from CH_4. The results of thermal experiments showed no conversion in six hours at 343°. In the presence of radiation, the reaction between CH_4 and C_2H_4 gave 3.1% conversion of CH_4 and 27.0% conversion of C_2H_4. The total reaction product contained, in mole per cent., 3.0 C_2H_6, 30.4 C_3H_8, 1.4 C_3H_6, 15.7 iso-C_4H_{10}, 21.2 C_4H_8, 12.0 iso-C_5H_{10}, and 5.8 C_6H_{12}. The radiation yield at these conditions is 1200 molecules of C_3 and higher molecular weight products per 100 ev. absorbed. At 426° both the thermal and radiation-induced reactions are appreciably rapid. For example, the thermal reaction gives in six hours CH_4 and C_2H_4 conversions of 5.0% and 80%, respectively. At this temperature a CH_4 conversion of 4.1% and a C_2H_4 conversion of 71.0% were obtained after two hours of irradiation. There is, therefore, a thermal reaction at 426° that is accelerated by radiation. Above 426° the thermal reaction is so rapid that acceleration by radiation is difficult to notice.

Work now in progress is designed to obtain detailed product composition *versus* conversion data for both the thermal and the radiation-induced reaction. A strict comparison at the same conditions and conversions is, of course, the best direct evidence one can use in deciding whether the radiation-induced reaction is an ionic or free radical chain process. However, it is very instructive to speculate on the meaning of the work reported here. If the reaction is indeed an ionic process, then it is to our knowledge the first reported ionic chain reaction of hydrocarbons at these conditions. If the process is free radical in nature, which is in our opinion more likely, then the above initiation step cannot be correct. This initiation rate should proceed at a rate given approximately by $10^{13}e^{-101{,}000/RT}$ (CH_4) molec. cc.$^{-1}$ sec.$^{-1}$, where 10^{13} is the normal unimolecular pre-exponential factor, (CH_4) is the methane concentration, and 101,000 kcal./mole is the CH_3–H bond strength. At about 50 atm. of methane this rate is negligibly small at 800°K., being in the order of 10^5–10^6 molec. cc.$^{-1}$. sec.$^{-1}$. Now the high *G* value obtained at 343° establishes the chain nature of the reaction and, furthermore, provides an approximate value for the chain length at the conditions of this work. However, the product of the above initiation rate and of the known chain length, which should give the value of the reaction rate, is smaller by many orders of magnitude than the observed thermal rate at 426°. Therefore, equation (1) cannot represent the initiation step.

However, a plausible initiation step can be written which removes the difficulty. This involves a bimolecular initiation between CH_4 and C_2H_4

$$CH_4 + C_2H_4 \longrightarrow CH_3\cdot + C_2H_5\cdot \qquad (1)$$

Such an initiation step is rarely discussed,[6] but is in fact highly likely since the reverse radical disproportionation reaction is well established and proceeds with zero or very low activation energy. Therefore, step (1) should have an activation energy not appreciably greater than its endothermicity. From available data on heats of formation,[6,7] the endothermicity of (1) is estimated to be 60 kcal./mole. Therefore, initiation by step (1) should proceed at an approximate rate of $10^{-10}\cdot e^{-60{,}000/RT}(CH_4)(C_2H_4)$, where 10^{-10} is the normal bimolecular collision number. At 50 atm. methane, 5 atm. ethylene, the initiation rate calculated from this expression is approximately that required to explain the measured thermal rate corresponding to the chain lengths estimated from this work.

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AN INVESTIGATION OF THE REACTION PRODUCTS OF BIS-CYCLOPENTADIENYLTITANIUM DICHLORIDE AND VARIOUS ALUMINUM ALKYLS BY ELECTRON SPIN RESONANCE

Sir:

Bis-cyclopentadienyl titanium dichloride was allowed to react with about a thousandfold excess of several aluminum alkyls in benzene solution and the electron spin resonance (e.s.r.) spectra of these solutions were observed at 3.2 cm. wave length and at 20°. The concentration of the titanium compound was between 10^{-4} and 10^{-3} molar in each case. The reactions with several aluminum alkyls were investigated: Me_3Al, Et_3Al, iso-Bu_3Al, Et_2AlCl, and $EtAlCl_2$. The tri-isobutyl system has been investigated previously by e.s.r.[1]

The nature of the e.s.r. spectrum was found to depend upon the aluminum alkyl which was allowed to react with the bis-cyclopentadienyltitanium dichloride. Furthermore, the e.s.r. spectrum of the $EtAlCl_2$ system was found to change with time (t). The intensity of the signal of this system was observed to increase slowly during the period t = 25 min. to t = 240 min. and had the appearance of Fig. 1c with an average g value of 1.975_3 at t = 90 min. The line width, ΔH, is 20.3 gauss. After a period of 51 days the appearance of the spectrum had changed to that shown in Fig. 1d. The spectrum shows six equally spaced and approximately equally intense components suggesting an isotropic hyperfine interaction with the Al^{27} nuclear moment ($I = 5/2$). The slight irregularity in the apparent intensities of the six hyperfine components is consistent with the presence of a small amount of the species producing the spectrum of Fig. 1c. At t = 8 days the e.s.r. spectrum had an appearance intermediate between Fig. 1c and 1d.

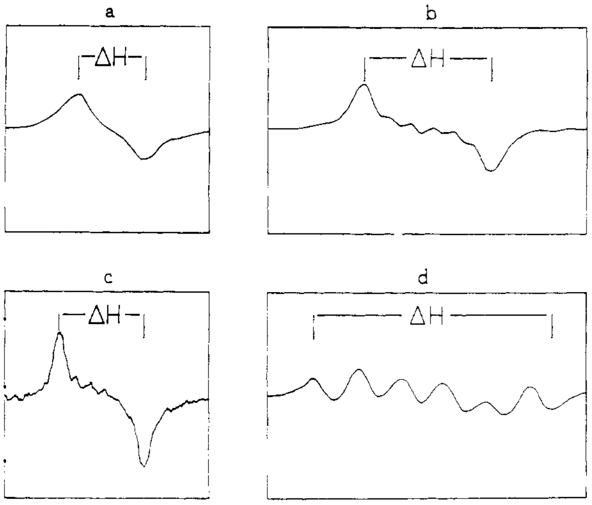

Fig. 1.—E.s. spectra at 3.2 cm. wave length and 20° of mixtures of Cp_2TiCl_2 in benzene with (a) Et_3Al, (b) Et_2AlCl, and (c) and (d) $EtAlCl_2$.

None of the other systems investigated showed a similar time dependence of the e.s.r. This observation indicates that the final paramagnetic product was already formed at the time of the first e.s.r. measurement: t = 1 day for Et_3Al, and t = 30 min. for Et_2AlCl. The e.s.r. spectra of the paramagnetic products of these reactions are shown in Fig. 1a and Fig. 1b, respectively. The e.s.r. spectra of the product of the reaction of the titanium compound with Me_3Al are essentially identical with those observed in the Et_3Al system. The e.s.r. spectrum given by the isoBu_3Al system was similar to that observed by Shilov, *et al.*,[1] and exhibits a hyperfine structure of eight equally spaced components with the approximate intensity relation 1:3:4:4:4:4:3:1.

The g values and resonance line widths, ΔH (as defined in Fig. 1), are given in Table I, at $t = \infty$.

TABLE I

Aluminum compound	Fig.	g-factor (±0.0005)	ΔH (gauss) (±0.5 gauss)
Me_3Al	..	1.976_2	13.3
Et_3Al	1a	1.976_0	10.7
Et_2AlCl	1b	1.975_0	20.3
$EtAlCl_2$	1d	1.974_5	38.7
Iso-Bu_3Al	..	1.987_2	28.0
Iso-Bu_3Al[1]	..	1.988	

The product of the reaction between Et_3Al and Cp_2TiCl_2 has been shown to be the compound $Cp_2TiCl_2AlEt_2$ (I), which has one unpaired electron.[2] A preliminary X-ray structure investigation showed that there is a tetrahedral disposition of groups around both the titanium and aluminum atoms and that these atoms are linked by chlorine bridges.[3] The final products of the reactions based upon Et_2AlCl and $EtAlCl_2$ are most probably the compounds $Cp_2TiCl_2AlEtCl$ (II) and $Cp_2TiCl_2AlCl_2$ (III), respectively, with structures similar to (I).[4] The rates of formation of these compounds from Cp_2TiCl_2 and the appropriate aluminum alkyl have been shown to be in the order $Et_3Al > Et_2AlCl > EtAlCl_2$, both by absorption spectral measurements in the visible region,[5,6] and by electrical conductivity and polarization measurements.[6] The first step in the reactions is the rapid formation (within a few minutes) of a complex containing aluminum, which is thought to be a diamagnetic species of the type $Cp_2TiCl_2 \cdot AlEt_2Cl$[5,6] or $Cp_2TiClEt \cdot AlEtCl_2$,[7] and which changes slowly to the final, paramagnetic, product. Our measurements of the $EtAlCl_2$ system are consistent with this view since we observe a slow increase in radical concentration after the initial mixing of the reactants. The spectra also indicate that more than one paramagnetic species is present.

The spectrum of the Et_2AlCl system contains poorly resolved hyperfine structure of six components. This is also consistent with a smaller hyperfine interaction with the Al^{27} nuclear moment. If we assume that ΔH is determined mainly by the hyperfine interaction with Al^{27}, then the increase of ΔH in the sequence I < II < III would indicate that the unpaired electron distribution favors the region of the Al atom in this same order. This interpretation is also consistent with the observation that ΔH for the paramagnetic compound $CpTiCl_2$, which contains no aluminum, is only about 6 gauss in solution and exhibits no hyperfine structure.[8] The unpaired electron distribution in the complex may be influenced by the inductive effect of the unbridged Cl atoms; the presence of this inductive effect is apparent from

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dipole moment measurements ($\mu_{II} = 6.4 \pm 0.5D$ and $\mu_I = 4.6 \pm 0.5D$).[6]

The compositions and structures of the products of the systems based upon Me_3Al and isoBu_3Al apparently are not known, but the formulations $Cp_2TiCl_2AlR_2$, where R = alkyl, may well apply. For R = Me, the e.s.r. spectrum is consistent with this assumption, whereas the large width of the spectrum observed in the case R = iso-Bu cannot be explained in this way, if the treatment used to explain the widths of the other spectra is correct. The hyperfine pattern given by the iso-Bu_3Al product is consistent with the interaction of the electron spin with the Al^{27} nuclear moment and with two equivalent protons which have equal coupling constants.[1] The e.s.r. results suggest that the final paramagnetic product of this reaction is not of the same structural type as given by the other aluminum alkyls which we have studied.

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1,1'-(TETRAMETHYLETHYLENE)-FERROCENE. OBLIQUITY AND N.M.R. IN BRIDGED FERROCENES

Sir:

We wish to report the preparation and properties of 1,1'-(tetramethylethylene)-ferrocene (I), containing an unusual two-carbon bridge linking the two cyclopentadienyl rings.

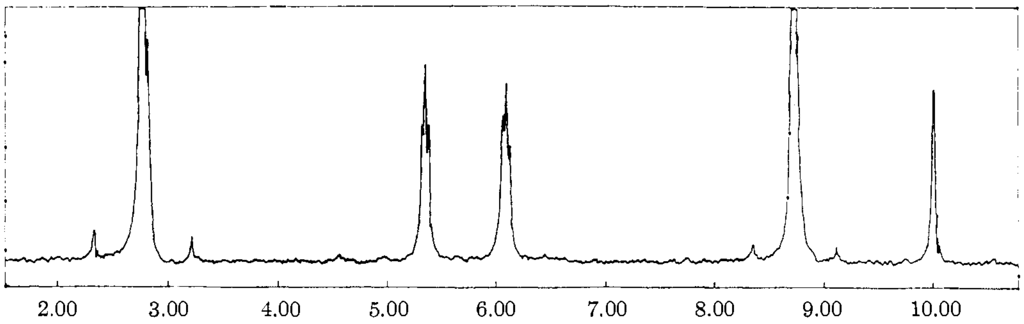

Fig. 1.

Treatment of 6,6-dimethylfulvene[1] with sodium metal dispersed in tetrahydrofuran, and then ferrous chloride, gave a mixture in which the major product (albeit in low yield) was the bridged compound (I); red crystals, sublimes 130° (8 mm.), m.p. 168–169° (crystal modification 129–130°) [*Anal.* Found: C, 71.83; H, 7.62; Fe, 20.68; mol. wt. (cryoscopic), 285].

The infrared spectrum of I is generally similar to that of 1,1'-diisopropylferrocene,[2] with bands at 3100, 917 and 850 cm.$^{-1}$ (alkylferrocene),[2] 1451, 1377 and 1367 cm.$^{-1}$ (*gem*-dimethyl).[3] Its ultraviolet spectrum is very similar to that of 1,1'-dimethylferrocene,[2] containing a weak maximum at 320 mμ (ϵ_{max} 492), a shoulder at 250 mμ (ϵ 4,920), and high end absorption (ϵ_{210} 13,600).

Although the ultraviolet and infrared spectra of I are characteristic of alkyl ferrocenes, the n.m.r. spectrum is not.[4] The n.m.r. spectrum of the close analog, 1,1'-diisopropylferrocene contains a single peak due to the ferrocene ring protons ($\tau = 5.97$),[5] together with the expected doublet ($\tau = 8.86$) and multiplet[4] ($\tau = 7.36$) due to methyl and methine protons, respectively. Similarly the spectrum of 2,3-diferrocenyl-2,3-dimethylbutane[6] contains three singlet peaks at $\tau = 8.69$ (methyl), 5.94 (unsubstituted ring) and 5.86 (substituted ring). The spectrum of I contains the expected methyl proton singlet ($\tau = 8.74$), but the ring protons are found in two widely separated triplets ($\tau = 6.11$ and 5.37; $J = 1.6$ c.s.). The considerable chemical shift is best explained as arising from the ring protons' unequal distance from the iron nucleus in a molecule where the rings are tilted; this interpretation is thus in accord with the mono-iron molecular weight above.

Since protons close to a transition metal nucleus have been shown to give n.m.r. peaks at relatively higher field in similar compounds (*cf.* cyclopentadienylcyclopentadienecobalt),[7] the ring 2-protons are assigned to the higher field peak ($\tau = 6.11$) and the ring 3-protons to the lower ($\tau = 5.37$).

Similar two-carbon bridged ferrocenes are formed from other fulvenes[8]; however, an alternative reaction path can predominate. Thus, the major product from treatment of cyclopentylidenecyclopentadiene (6,6-tetramethylenefulvene)[9] with sodium, then ferrous chloride, is 1,1'-di-(1-cyclopentenyl)-ferrocene (II), m.p. 108–109° [*Anal.*

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