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ELECTRON SPIN RESONANCE STUDY ON FREE RADICALS FROM SATURATED HYDROCARBONS AND ANTIMONY PENTACHLORIDE

K. Fukui, T. Kawamura, T. Masuda and K. Morokuma
Department of Fuel Chemistry, Faculty of Engineering
Kyoto University, Kyoto, Japan

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Extensive electron spin resonance (e.s.r.) studies have long been carried out on aromatic positive ion radicals obtained by adding strong Lewis acids to polynuclear aromatic hydrocarbons (1). Recently Adams and Nicksic (2) found free radicals by e.s.r. in Friedel-Crafts reactions of benzene and alkyl chlorides catalysed with aluminium chloride.

We observed e.s.r. absorption in products of the reaction of saturated hydrocarbons* with antimony pentachloride. When a carbon tetrachloride solution of antimony pentachloride was added at the room temperature to a saturated hydrocarbon (3) bearing a tert-hydrogen atom, the mixture became gradually turbid from the air-solution boundary and after few minutes separated a viscous, deep brown liquid phase with violent releasing of bubbles of hydrogen chloride. Hydrocarbons with no tert-hydrogen atom also reacted with the reagent but showed an induction period

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* Hydrocarbons were ascertained not to be contaminated with aromatic or conjugated diene hydrocarbons by U. V. spectra.

about 100 times longer than those with a tert-hydrogen atom and the reaction proceeded very slowly.

E.s.r. absorption was observed when the brown tarry phase was inserted in the microwave cavity, and it continued about 3 hours after the reaction. The turbid mixture did not show any e.s.r. spectrum. Data of e.s.r. spectra are tabulated in TABLE I.

TABLE I

Hydrocarbon	E.s.r. spectra		Radical concentration Mole/l
	Structure	ΔH_{msl} G	
2-Methylbutane	Complicated h.f.s.	0.5	$10^{-3} \sim 10^{-4}$
2-Methylpentane	Well resolved h.f.s.	0.5	7×10^{-4}
3-Methylpentane	Well resolved h.f.s.	0.5	7×10^{-4}
2,2,4-Trimethylpentane	Resolved h.f.s.	0.9	$10^{-4} \sim 10^{-5}$
2,2,5-Trimethylhexane	Unresolved h.f.s.	--	2×10^{-4}
Methylcyclohexane	A broad single line	12	$< 10^{-5}$
n-Heptane	A broad single line	21	10^{-5}
4-Methyl-2-pentene	A very weak broad single line	--	$< 10^{-5}$

ΔH_{msl} : The line width measured between max. and min. on derivatives.

The products obtained from 2-methylpentane and from 3-methylpentane in the air showed entirely the same, well resolved spectra (FIG.I) consisting of 7 lines with a splitting constant of 11.4 G and with an intensity ratio of (7 : 30 : 75 : 100 : 73 : 30 : 7), and each of which splitted further into 7 lines with a splitting constant of 4.4 G and with an intensity ratio of (13 : 41 : 82 : 100 : 82 : 42 : 13). These data may be explained as follows :

an odd electron couples with 6 protons with a coupling constant of 11.4 G (the theoretical intensity ratio; 5 : 30 : 75 : 100 : 75 : 30 : 5) and 8 protons with a coupling constant of 4.4 G (the theoretical intensity ratio; 1.4 : 11.4 : 40 : 80 : 100 : 80 : 40 : 11.4 : 1.4 and the outermost peaks were hidden in the noise).

The g-value of the radicals both from 2- and 3-methylpentane were 2.0027, which would mean that the odd electron has no interaction with a chlorine atom.

The reaction product from isooctane (2,2,4-trimethylpentane) also showed an e.s.r. spectrum which had the same h.f.s. mentioned above, but its radical concentration was much smaller. The reaction product from 2-methylbutane showed a resolved , but more complicated h.f.s., which suggested two or more radical species were involved.

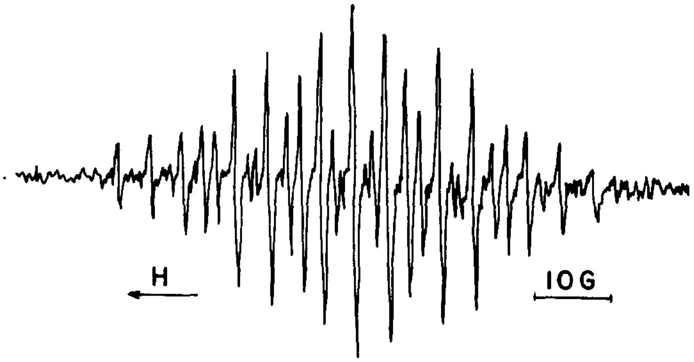

FIG.I

First derivative of the e.s.r. absorption vs. magnetic field of the product from 3-methylpentane. (Volume ratio C_6H_{14} : CCl_4 : $SbCl_5$=3 : 1 : 3. Reacted in the air.)

The reaction product from 3-methylpentane obtained in the oxygen-free and water-free nitrogen atmosphere (I) showed an e.s.r. spectrum of a broad single line absorption with a weak h.f.s., some components of which coincided with the above-mentioned h.f.s. of the product of the reaction in the air (II). On exposing (I) to the air, its e.s.r. spectrum changed immediately to the same spectrum that was observed in (II). The evacuation of the air out of the sample tube to 10^{-5}mmHg caused no change in the e.s.r. spectrum of (II).

These experiments seem to show that there are some radical species in (I) and one of them is stable in the air, and that in this radical the odd electron has no interaction with an oxygen atom.

It is said that the tarry lower layer formed by the reaction of alkanes and aluminum chloride consists of addition compounds of complex unsaturated hydrocarbons with aluminum chroride (4). The tarry phase which we obtained would also possess unsaturated structures, and the radical which showed the e.s.r. spectrum would be one of radical cations of these unsaturated hydrocarbons. To find the radical structure, we examined several radical cations of hydrocarbons with McLachlan's spin correlation procedure (5). A most likely structure, its spin distribution, and coupling constants of protons are shown in FIG.II, although we are not able to elucidate the mechanism of the formation of such a complicated, but single, species. Spin densities are calculated by McLachlan' procedure with $\lambda=1$. Coupling constants of protons are calculated with $A_H=Q_{CCH_3}\rho_C$, $Q_{CCH_3}=27G$.

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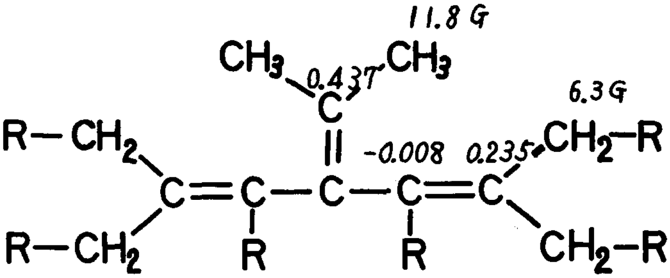

FIG.II

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