FREE RADICALS IN FRIEDEL–CRAFTS REACTIONS

Sir:

The Friedel–Crafts alkylation reaction catalyzed by aluminum chloride has been explained on the basis of an ionic mechanism. We recently observed electron paramagnetic resonance (e.p.r.) absorption in liquids undergoing this reaction. The gradual increase in the e.p.r. absorption during the reaction suggests that free radicals either may be intermediates in the reaction mechanism or associated with one or more of the reaction products. Free radicals have been observed in polynuclear aromatic compounds treated with aluminum chloride.[1,2]

A conventional Varian V-4500 EPR spectrometer with 100-kc. field modulation was used to detect the absorption. Frequency and field were measured with a Varian F-8 Nuclear Fluxmeter, a Hewlett-Packard 524C Electronic Counter, and a Hewlett-Packard 540B Transfer Oscillator. The spectra were taken in a Varian V-4012A Electromagnet with flux stabilizer. The methods of Blois, Brown, and Maling[3] were used in the quantitative measurements. The field inhomogeneity between the fluxmeter probe and the radical sample in the microwave cavity was corrected by measuring the well-known g-value of 1,4-benzosemiquinone[3] for each experimental arrangement.

To reduce the number of reactant and catalyst variables in the reaction, benzene and aluminum chloride were used in combination with various alkylating agents. An aluminum-chloride-in-benzene solution was prepared by boiling preboiled benzene in the presence of solid anhydrous aluminum chloride until the liquid turned light yellow. The solution was decanted and chilled to just above its freezing point. It showed no e.p.r. absorption. The chilled alkylating agent was mixed with the solution in a 1:10 volume ratio. The use of almost any alkyl halide or olefin gave e.p.r. absorption during and often after reaction. The alkylating agent plus aluminum chloride alone gave a much wider and less intense absorption peak than when benzene was present. Quantitative e.p.r. measurements were made on alkylation reactions of four alkyl halides: 1,2-dichloroethane, 1-chlorobutane, dichloromethane, benzyl chloride.

A sample of the chilled reaction mixture was placed in the microwave cavity, and the magnetic field was swept repeatedly over the resonance. As the mixture approached room temperature, the reaction produced a separate, highly colored phase in the bottom of the sample tube, releasing bubbles of hydrogen chloride from the interface of the two solution phases. E.p.r. absorption could be obtained only when the interface and the highly colored phase were in the microwave cavity.

TABLE I

FREE RADICALS IN $AlCl_3$ CATALYZED ALKYLATION OF BENZENE

Alkylating agent	g-Value	Line width, gauss
1-Chlorobutane	2.00251 ± 0.00008	0.17
1,2-Dichloroethane	2.00257 ± .00012	.43
Dichloromethane	2.00251 ± .00009	.21
Benzyl chloride	2.00256 ± .00010	.23

The e.p.r. spectra of the 1,2-dichloroethane and 1-chlorobutane reactions followed the same pattern. A single, narrow line was observed which grew in intensity until the hydrogen chloride no longer bubbled off. In the case of 1-chlorobutane, the line was unchanged in intensity or width when the sample stood overnight open to the air at room temperature. Assuming all radicals to be in the highly colored phase, the spin concentration was estimated to be 10^{-6} molar at the end of the 1-chlorobutane reaction.

During the reactions of dichloromethane and benzyl chloride, the narrow single line appeared and grew in intensity. Then a hyperfine splitting spectrum of 19 lines, centered on the narrow line, emerged from the noise. When the sample was exposed to the air at room temperature overnight, the hyperfine spectrum showed typical oxygen broadening.

The line widths and g-values for the narrow lines are given in the table. The lines probably were broadened by excessive field modulation due to poor signal-to-noise ratios.

In the case of 1-chlorobutane, the signal-to-noise ratio reached 250, permitting a search for C^{13} splitting. No splitting was found within 20 gauss of the single line.

On the basis of the work of Blois, Brown, and Maling,[3] the g-values we obtained indicate that the free radicals being observed are hydrocarbons containing no oxygen or chlorine atoms. The nature of the reactants makes it probable that the hydrocarbon free radical is aromatic. The narrow line width and no hyperfine splitting in such a complex system will require for their explanation rather bold assumptions. We are reluctant to offer such assumptions at this time in the absence of quantitative calculations. Further work is in progress.

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EFFECT OF AMMONIA ON THE RADIATION-INDUCED POLYMERIZATION OF CYCLOPENTADIENE AT −78°[1]

Sir:

Ionic polymerization often is initiated by proton transfer from a Brönsted acid to the monomer. Ionization of molecules by electron impact gives the parent molecule-ion, which displays the chemical properties of a charged free radical.[2,3] Molecule-ions derived from the hydrides of carbon, nitrogen, oxygen, and other elements are appropriately described as protonated free radicals.[4]

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(4) In the case of the parent molecule-ion obtained from unsaturated hydrocarbons, we make the formal identity: $-CH\overset{+\cdot}{-}CH-CH_2- = H^+(-\overset{\circ}{C}H-CH=CH-)$; *cf.* Ff. Williams, *J. Am. Chem. Soc.*, **84**, 2895 (1962).