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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[1] H. M. Buck, W. Bloemhoff and L. J. Oosterhoff, *Tetrahedron Letters*, **No. 9**, 5 (1960).

[2] J. J. Rooney and R. C. Pink, *Proc. Chem. Soc.*, 142 (1961).

[3] M. S. Blois, Jr., H. W. Brown and J. E. Maling, Ninth Colloque Ampere, September, 1960.

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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[1] This research is supported by A.E.C. Contract No. AT-(40-1-)-2968.

[2] H. Eyring, J. O. Hirschfelder and H. S. Taylor, *J. Chem. Phys.*, **4**, 479 (1936).

[3] W. F. Libby, *ibid.*, **35**, 1714 (1961).

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

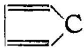
Examples are known where the molecule-ion derived from olefinic hydrocarbons reacts with the neutral olefin to form the even-electron carbonium ion,[5] *i.e.*, the protonated olefin. Elementary considerations suggest that any reaction characteristic of *protonated* intermediates should be subject to inhibition or modification in the presence of a strong Brönsted base. We wish to report an unambiguous example of this effect which proves, *ipso facto*, that the radiation-induced polymerization of cyclopentadiene is an *ionic* reaction.

Cyclopentadiene has been found to polymerize reproducibly when irradiated at −78° with cobalt-60 gamma-rays. The preparative technique follows the description given for other monomers,[6] except for double distillation *in vacuo* below −40°, and subsequent storage[7] at −78°. By this procedure, the spontaneous formation of dimer was reduced to insignificant proportions. Irradiation beyond a dose of 6.0×10^{17} e.V.g.$^{-1}$, corresponding to 2.0% conversion, results in gel formation. The yield of polymer is linear with irradiation dose up to about 20% conversion ($G(\text{—}C_5H_6) = 25{,}000$). At doses exceeding 5.0×10^{19} e.V.g.$^{-1}$, the pure monomer is converted to a firm rubber, impervious to solvents. The extreme potency of ammonia in reducing the polymerization yield is shown by the representative data of Table I.

TABLE I

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

Ammonia concentration, mole fraction $\times 10^3$	Dose $\times 10^{-18}$, e.V.g.$^{-1}$	Conversion to polymer, %
None	1.0	3.4
None	5.0	15.2
None	10.0	25.5
1.8	50.0	0.29
0.20	50.0	0.64
.012	50.0	1.30
.0054	50.0	2.7

The interpretation of the action of ammonia is clarified by several points: (a) ammonia has a high proton affinity, $P_{NH_3} = 202$ kcal./mole,[8] this being the reason why ammonia acts as a very efficient base for ion-molecule reactions involving proton transfer from hydrocarbon ions.[9] (b) Ammonia has a large dipole moment ($\mu = 1.46$ debye) which allows for strong ion-dipole interaction. (c) The ionization potential of ammonia ($I_{NH_3} = 234$ kcal./mole)[10] exceeds that of cyclopentadiene ($I_{C_5H_6} = 198$ kcal./mole)[11]; hence charge transfer from cyclopentadiene to ammonia is inapplicable. (d) An efficient reaction of a *neutral* hydrocarbon free radical with ammonia by hydrogen atom abstraction is precluded in this system by the fact that $D_{H\text{-}NH_2} = 106$ kcal./mole,[12] which must surely exceed the CH–H bond dissociation energy in cyclopentadiene. In any event, hydrogen atom transfer reactions with ammonia would lead to chain transfer rather than the termination which must apply here.

The preceding facts and arguments, taken together with the knowledge that cyclopentadiene polymerization is effected readily by a variety of Friedel–Crafts ionic catalysts,[13] compel the conclusion that ammonia interferes at such low concentrations by virtue of its possession of an unshared pair of electrons. In other words, the basicity of ammonia renders it an excellent ion scavenger. Apart from simple proton transfer to ammonia, we do not rule out the possible ammonolysis of a carbonium-ion intermediate, *viz.*, $R^+ + 2NH_3 \rightarrow R\text{-}NH_2 + NH_4^+$.

These results suggest the possible utility of ammonia as an ion scavenger in the radiation chemistry of hydrocarbon gases and liquids, especially where chain reactions of unknown mechanism are prevalent. Further work is in hand, and will be reported in due course.

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(14) Undergraduate research participant (summer 1962) supported by National Science Foundation under grant G-21638.

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TRANSFORMATIONS OF EBURICOIC ACID. III.[1] A-NOR-3,11-DIKETO-14-METHYLPREGNANE DERIVATIVES

Sir:

In a previous communication from this laboratory[2] we reported the degradation of eburicoic acid to Δ^8-14-methylpregnene derivatives *via* the α-pyrone I. We now wish to describe the conversion of this key intermediate to 14-methyl-A-nor-3-ketopregnanes and Δ^5-pregnenes. Related compounds such as $\Delta^{3(5)}$-A-norpregnene-2,20-dione[3] have been shown to possess anti-androgenic activity of a high order.[4]

Oxidation of the pyrone I with $KMnO_4$ in acetone[5] furnished in 40% yield the Δ^8-diketo acid IIa, m.p. 252–255°; $[\alpha]_D + 85°$[6]; λ_{max}^{alc} 268 mμ ($\epsilon = 9{,}100$). Its methyl ester, m.p. 178–179°; $[\alpha]_D + 88°$; λ_{max}^{alc} 268 mμ ($\epsilon = 9{,}400$); on reduction with zinc and acetic acid gave the saturated diketo ester IIb, m.p. 262°; $[\alpha]_D + 70°$; which was converted with ethanedithiol in BF_3-etherate to the 7-thioethylene ketal IIc, m.p. 211–212°; $[\alpha]_D + 19°$; and thence with sponge nickel in ethanol to

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(6) Rotations in chloroform at 23°, unless indicated otherwise.