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LETTERS TO THE EDITORS

Electron Spin Resonance of Olefin and Benzene Free Radicals on Synthetic Zeolites

Recently Stamires and Turkevich (*1*) reported observing ESR spectra arising from perylene and other molecules of low ionization potential (about 7.2 eV) adsorbed at room temperature on decationized Y-type zeolites. Rooney and Pink (*2*) also have observed ESR signals from molecules of low ionization potential adsorbed on silica-alumina but were unable to observe signals from benzene or methyl-substituted benzenes. We report here ESR spectra arising from compounds whose ionization potentials are more than 2 eV (46 kcal) higher than those previously reported. Our observations include olefins, benzene, and methyl-substituted benzenes adsorbed on rare earth and calcium-exchanged Y zeolites and cerium-exchanged X zeolite.

A conventional Varian V-4502 EPR spectrometer with 100 kc/sec field modulation was used in these experiments. The instrument is fitted with a Varian Fieldial Magnet Field Regulator V-FR 2503 so that approximate "g" values are readily obtained. Linewidths and line separation measurements were made by reference to a dilute basic solution of Fremy's salt in one-half of the dual cavity. All signals observed were in the $g = 2.0$ region although accurate measurements have not been made at this time.

The solids used in this study were prepared by ion exchange of the sodium zeolites with either mixed rare earth nitrates, cerium nitrate, or calcium chloride. The zeolites were then washed, thoroughly dried, and activated by heating in a stream of dry air at 500°C. Samples for ESR examination were prepared by dissolving appropriate quantities (1 mg to 0.2 g) of the hydrocarbon to be studied in 2 cc of carbon tetrachloride in a small vial and then adding 0.3–0.5 g catalyst. Addition of carbon tetrachloride to the catalyst prior to the addition of the hydrocarbon was equally satisfactory. Upon addition of the catalyst, strong colors were developed which were green, brown, or black depending on the particular hydrocarbon chosen. Transfer to 4-mm quartz ESR sample tubes was effected by the use of a drawn eyedropper. No difference in the ESR spectrum was observed when samples were prepared from degassed carbon tetrachloride-hydrocarbon solutions added under vacuum to freshly activated catalyst so that the simpler procedure described above was routinely used.

The dry catalysts gave no detectable ESR signal; however, when either heptane or carbon tetrachloride was added a very weak unsymmetrical line at $g = 2.0$ was observed and a rather dark gray color developed. The cause of this line has not been investigated further; however, it is so weak that it does not affect the appearance of the spectra produced by olefins or aromatics. Spectra obtained with neat olefins gave spectra similar to those obtained from carbon tetrachloride solution although somewhat broadened due to the high spin concentration developed.

In Fig. 1 the spectra from pentene-2 and octene-1, adsorbed on rare-earth–exchanged Y zeolite from carbon tetrachloride are shown. The line intensities observed for the pentene-2 case agree with those expected from six equivalent protons giving rise to a seven-line spectrum having a binomial distribution of intensities, namely, 1,6,15,20,15,6,1. Theoretical spectra were calculated assuming a Gaussian line shape for the individual lines, and taking the hyperfine splitting constant, measured from the spectra, as 13.5 gauss. The linewidth was systematically varied until calculated intensities agreed with those observed. The linewidth giving the best agreement with experiment was 9.72 gauss.

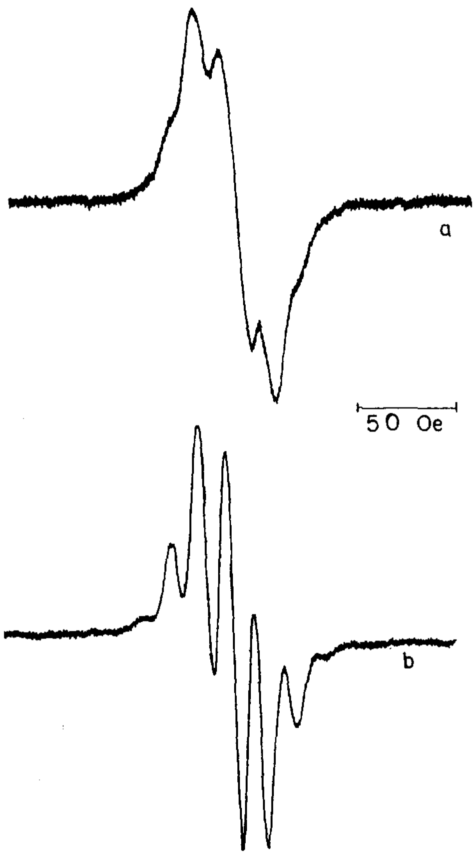

FIG. 1. Octene-1 (a) and pentene-2 (b) adsorbed from carbon tetrachloride on rare-earth-exchanged Y molecular sieve.

The linewidth to hyperfine splitting ratio (β) is 0.72. The experimental spectrum compares favorably with the theoretical spectrum calculated by Lebedev *et al.* (*3a*) for six equivalent protons having $\beta = 0.71$.

Extensive calculations have not been carried out on octene-1; however, the spectrum shown in Fig. 1 agrees quite well with a five-line spectrum (*3b*) of intensity ratios 1,4,6,4,1, and $\beta = 1.01$. The measured hyperfine splitting is 12.0 gauss, which gives a linewidth of 12.12 gauss. Spectra obtained from 2-methylbutene-2 and 4-methylpentene-2 (not shown) are poorly resolved seven-line and five-line patterns, respectively, of very near binomial intensity distribution.

When perylene was adsorbed on the rare-earth or cerium-exchanged zeolites and on decationized Y and X zeolites the same spectrum was observed as previously reported by Stamires and Turkevich (*1*) and by Rooney and Pink (*2*). While the perylene spectrum has been interpreted as arising from a radical formed by simple electron abstraction, the interpretation of the olefin spectra reported here does not appear to be so straightforward. The magnitude of the hyperfine splitting observed for the olefins studied here is nearly one-half the value found for the methyl group in ethyl radicals (*4*), viz. 26.87 gauss. This is interpreted to mean, in the olefin case, that the electron is delocalized over two carbon atoms. The binomial distribution of intensities observed requires interaction with six equivalent protons for pentene-2 and 2-methylbutene-2, and four equivalent protons for octene-1 and 4-methylpentene-2. With these olefins simple electron abstraction does not generate a radical which would be expected to have a seven- or five-line spectra and accordingly is not a satisfactory mechanism to explain the results reported here.

In view of the difficulty in interpreting all of the spectra on the basis of an electron abstraction mechanism of reaction, the question of isomerization or reaction of the olefins on contact with the surface was studied. Analysis of the supernatant liquid by vapor-phase chromatography indicated that after a week's contact with the catalyst less than 2% of pentene-1 or pentene-2 had been isomerized to pentene-2 or pentene-1, respectively. However, a small amount of pentene-2 polymer was recovered from the catalyst, and this polymer generated the same ESR spectrum as pentene-2 when added to fresh catalyst. Analysis by NMR showed that after 4 days only traces of octene-1 had been converted to a new olefin, probably octene-2, on the basis of the new lines observed. These data suggest that the observed radicals are probably not derived from an isomerized product, but from either a polymer or the initial monomer. Other mechanisms of reaction based on hydride ion additions and abstractions, hydrogen atom additions, and isomerizations are being examined. At the present time, no one hypothesis is consistent with all the spectra observed.

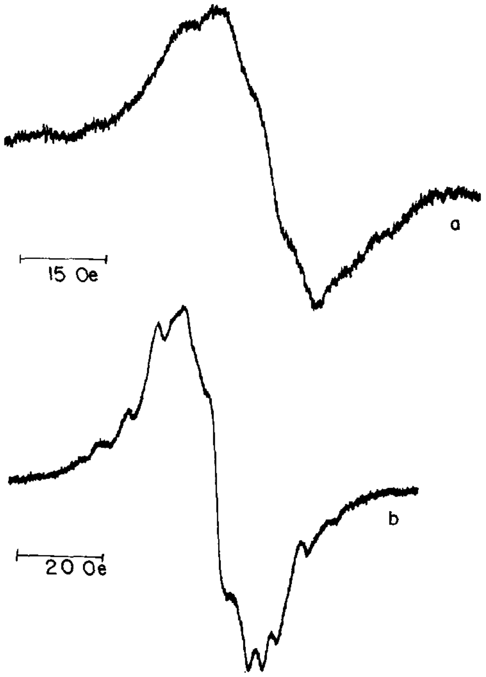

FIG. 2. Benzene (a) adsorbed neat on calcium-exchanged Y molecular sieve and pentamethylbenzene (b) adsorbed from carbon tetrachloride on rare-earth–exchanged molecular sieve.

In Fig. 2, the spectra from benzene and pentamethylbenzene are shown. With benzene, it was not possible to observe hyperfine structure on the rare-earth or cerium-exchanged sieves even at very low concentrations. However, when benzene is adsorbed neat on the calcium-exchanged sieve the hyperfine structure is just barely visible. The hyperfine splitting is 5.0 ± 0.5 gauss which agrees well with results obtained on hydrocarbons of lower ionization potential in sulfuric acid. With pentamethylbenzene, 11 lines can be seen, which undoubtedly arise from interaction of the unpaired electron with methyl groups via hyperconjugation. The line separations near the center are 3.0 gauss and in the wings 5.8 gauss. Strong but poorly resolved spectra have also been observed for toluene and *m*-xylene. Work is continuing with these and other hydrocarbons in an effort to improve the resolution of the spectra, to establish an upper limit to ionization potential, and to gain an understanding of the nature of the catalysts, and of the nature of the radicals formed.

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