

The Electron Spin Resonance Spectra of Radicals obtained by the Addition of Amino and Hydroxyl Radicals to Alkenes

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COFFMAN and co-workers¹ have reported the reaction of amino-radicals with olefins and have postulated as a first step the formation of a free-radical species H_2N-A^\bullet , in which A represents a unit of composition corresponding to that of the olefin employed. The addition of NH_2^\bullet radicals, generated by the reaction between titanium(III) and hydroxylamine, to a range of vinyl compounds can be conveniently studied^{2,3} by means of electron spin resonance techniques.

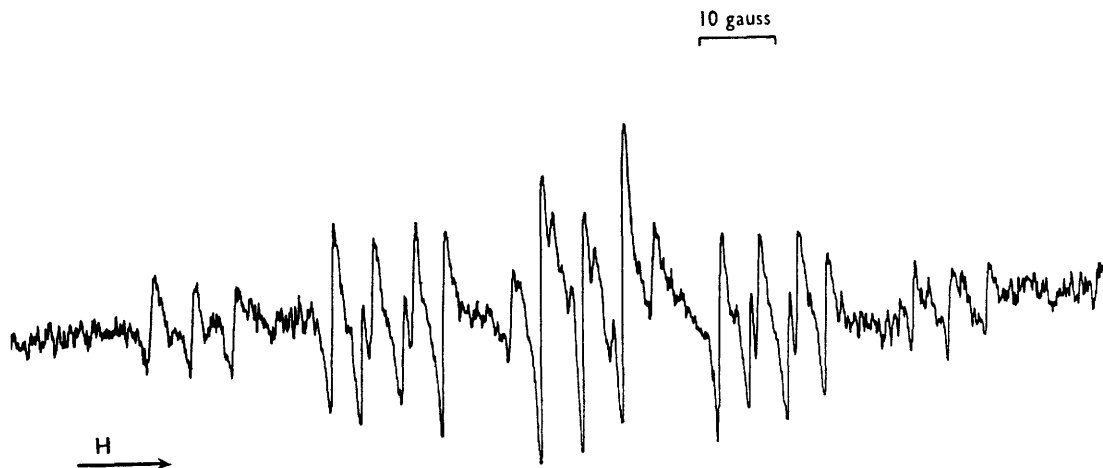
We have been examining simple olefinic systems and now report some of our results, obtained by a method closely similar to Fischer's.² We have identified the radicals produced by addition to ethylene.

When an acidified (0.13M- H_2SO_4) aqueous solution of titanous chloride ($\sim 0.02M$) and a solution of hydroxylamine hydrochloride ($\sim 0.5M$) saturated at 25° with ethylene ($\sim 0.01M$) were allowed to mix rapidly at the cavity of a 100 kc

¹ C. J. Albisetti, D. D. Coffman, F. W. Hoover, E. L. Jenner, and W. E. Mochel, *J. Amer. Chem. Soc.*, 1959, **81**, 1489.

² C. Corvaja, H. Fischer, and G. Giacometti, *Z. phys. Chem. (Frankfurt)*, 1965, **45**, 1.

³ H. Fischer, *Z. Naturforsch.*, 1964, **19a**, 866.



Varian V4500 - 10A E.S.R. spectrometer (following the technique of Dixon and Norman⁴) the spectrum shown in the Figure was obtained.

This spectrum consists of a well defined nitrogen triplet of splitting 4.8 gauss and two sets of 1 : 2 : 1 triplets of respectively, 21.9 gauss and 25.6 gauss separation, arising from two sets of two equivalent protons. Exactly the same spectrum is obtained when a hydrogen atom is abstracted from ethylamine by OH, generated from the H₂O₂-titanium-(III) system by the method of Dixon and Norman,⁴ who were unable⁵ to detect this radical. From their results for n-propylamine we suggest that the spectrum now observed, both by hydrogen abstraction from ethylamine and by NH₂• addition to ethylene, corresponds to the same radical •CH₂CH₂NH₂ or its protonated species. The observed proton hyperfine structure is assigned to the hydrogens of the methylene groups.

In a similar way when an acidified aqueous solution of titanous chloride and an approximately 0.05M solution of hydrogen peroxide in water saturated at 25° with ethylene were brought

together rapidly, a well-resolved spectrum was obtained corresponding to the addition of a hydroxyl radical to the double bond of the olefin. This spectrum consisted of two triplets (1 : 2 : 1) of respective coupling constants 20.7 gauss and 26.4 gauss.

The hyperfine coupling constants obtained for these radicals agree well with previous observations on radicals of this type^{3,5} and may be assigned by analogy. The absence of hyperfine structure from the protons attached to the nitrogen atom indicates either that protonated species are exchanging rapidly in solution or that their coupling constants are too small to be detected, as in the case of hydroxylated radicals.⁴

We have also observed similar e.s.r. spectra from other simple alkenes, in particular propene, but-2-ene, and butadiene. However, the complexity of the spectra obtained arising through isomer distribution requires further investigation and these results will be reported later.

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⁴ W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1963, 3119.

⁵ W. T. Dixon, R. O. C. Norman, and A. L. Buley, *J. Chem. Soc.*, 1964, 3625.