Electron Spin Resonance Studies of Primary Processes in Radiation-induced Reactions

IV. Evidence for Cation Formation in 1,3-Butadiene-1,1,4,4-d_4 Adsorbed on Silica Gel

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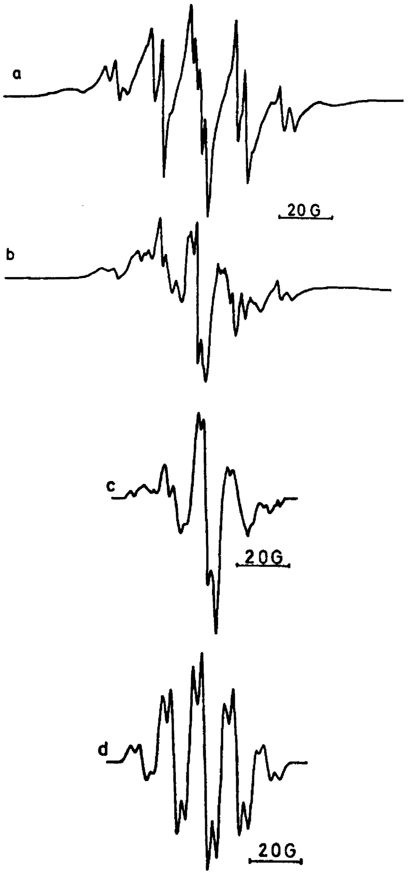

Fig. 1. ESR spectrum of 0.13 mol % of 1,3-butadiene on silica gel following γ-irradiation at 77 K to 8×10^5 rad, measured at 153 K. a, with 0.8 mol % of TEA; b, without TEA; c, component present without TEA which decays at 195 K; d, the simulated spectrum using as parameters four $a_H = 11.4$ G two $a_H = 3.2$ G and a Gaussian line width $\Delta H = 2.9$ G.

In the previous work, 1,3-butadiene adsorbed on silica gel was investigated by ESR following γ-irradiation.[1] The thermally unstable ESR signal observed at low concentrations of butadiene (0.1 mol %) on the silica gel has been assigned to the cation radical of butadiene. This radical has not been identified before by ESR spectroscopy. The aim of this paper is to support the identification of the butadiene cation radical by using 1,3-butadiene-1,1,4,4-d_4 and by the effect of a cation scavenger.

The procedure for purifying and drying the 1,3-butadiene was the same as in the previous work.[1] Triethylamine (TEA) was purified by distillation and was dried under reduced pressure with Na-K alloy in a pyrex glass ampoule. Silica gel was dried at 650°C for 24 h. The procedures for sample preparation and irradiation were as described previously.[1] The ESR spectra were measured with a Varian E-9 X-band spectrometer employing 100 kHz magnetic field modulation at a microwave power of 0.06 mW.

In the presence of 0.8 mol % TEA the spectrum from a sample containing 0.13 mol % butadiene did not contain any indication of the component containing five lines separated by 11 G which has previously been observed in the absence of TEA.[1] This component was obtained by subtraction of the background signal remaining at 195 K from the spectrum recorded in the absence of TEA, (Fig. 1c). The theoretical positions and intensities of the hyperfine lines are indicated in Fig. 1d. These spectra were obtained after photobleaching; this treatment removes the $g = 2.0070$ signal from a positive hole centre in the silica gel. This centre was present at 77 K only in the absence of TEA.

A sample containing 0.13 mol % butadiene-d_4 yielded at 77 K a spectrum which contained several lines separated by 1.75 G. After photobleaching, the spectral resolution increased, due to the decay of the $g = 2.0070$ silica gel signal. The intensity of the remaining absorption is not affected by photobleaching. At 153 K the spectrum

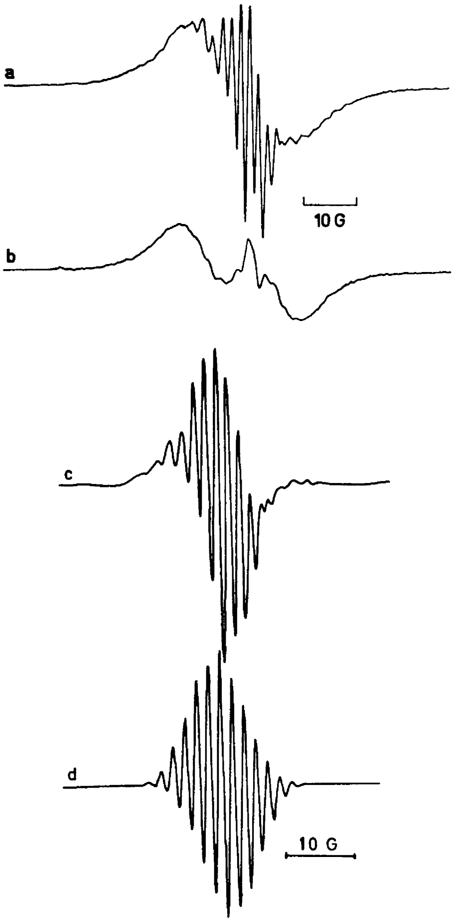

Fig. 2. ESR spectrum of 0.13 mol % of 1,3-butadiene-1,1,4,4-d_4 on silica gel following γ-irradiation at 77 K to 8×10^5 rad, measured at 153 K. a, before heating the sample to 203 K; b, after heating the sample to 203 K; c, the difference spectrum obtained by subtraction of Fig. 2a from Fig. 2b; d, the simulated spectrum using as parameters two $a_H = 3.16$ G, four $a_D = 1.74$ G and a Gaussian line width $\Delta H = 1.00$ G.

of Fig. 2a was obtained. The line profile is the same as that at 77 K after photobleaching. The central part of the spectrum disappeared when the temperature was increased to 203 K. The broad background in Fig. 2b was subtracted and the spectrum of Fig. 2c was then obtained. The simulated line profile shown in Fig. 2d was obtained assuming interactions with two equivalent protons with $a_H = 3.16$ G and four equivalent deuterons with $a_D = 1.74$ G. The Gaussian derivative line width is 1.00 G.

The ionization potential of TEA (7.50 eV) [2] is lower than that of butadiene (9.18 eV).[3] Thus TEA can act as a positive charge scavenger. The absence of the quintet in the presence of TEA strongly suggests that the associated species is formed by a positive charge transfer mechanism.

A theoretical estimate yields $a_1 = 11.4$ G and $a_2 = 3.16$ G for the proton splitting constants [1] of the butadiene cation. The deuteron has a nuclear spin $I = 1$, yielding a triplet of lines with a hyperfine splitting reduced by a factor g_D/g_H compared with that of the proton. Accordingly the coupling constant of the deuterons in butadiene-d_4 is estimated to be 1.74 G. The good agreement between the experimental spectrum, Fig. 2c, and the simulated, Fig. 2d, shows that the theoretical estimates for a_1 and a_2 are close to the experimental values. These findings give strong support to the assignment to the butadiene cation.

The fact that cation signal strength is not affected by the decay of the $g = 2.0070$ signal which accompanies photobleaching shows that a transfer reaction following photobleaching does not occur. The hole centre and the cation might form in competing reactions with positive charge created by ionization during the irradiation. This is supported by the absence of hole signal in the presence of TEA, which scavenges positive charge more efficiently than does butadiene.

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