E.S.R. Studies of the Formation of Hydrocarbon Radicals on the Clean Surfaces of Evaporated Ionic Solids

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Cyclohexyl and allyl radicals are detected by e.s.r. spectroscopy when cyclohexane and 2,5-dimethylhex-3-ene are deposited on to the uncontaminated, continuously renewed surface of sodium chloride evaporated on to the cold surface of a rotating cryostat at 77 K.

Very large electrostatic fields (*ca.* 10^7 V cm^{-1}) exist on the surfaces of ionic solids.[1,2] These can affect the course of heterogeneous catalytic reactions[1,3] and also result in the formation of cationic and anionic radicals (requiring energies >870 kJ mol^{-1}) when aromatic, aliphatic, and inorganic substrates such as O_2 and CO_2 are used.[4] Methyl radicals showing restricted rotation have been detected by e.s.r. following the u.v. photolysis of methyl iodide adsorbed on silica gel at 77 K.[5] However, there have been no reports of the formation of hydrocarbon radicals on the surfaces of such solids in the absence of photolytic or radiolytic excitation, although cleavage of the C=O bond in carbon monoxide adsorbed on metal surfaces has been observed by *X*-ray and ultraviolet photoelectron spectroscopy (XPS and UPS).[6] This may be due partly to the rapidity with which the surfaces are contaminated by traces of H_2O, O_2, and other gaseous impurities. The rotating cryostat provides a way of circumventing this problem of surface contamination without recourse to ultra high vacuum techniques.

The technique has been described in detail elsewhere,[7,8] but for the experiments described here the technique was used as follows. A stainless steel drum containing liquid nitrogen was set spinning at *ca.* 2000 r.p.m. in a high vacuum chamber ($<10^{-6}$ Torr). Sodium chloride was vapourised in a resistively heated molybdenum furnace (*ca.* 900 °C) and the vapour condensed on to the cold moving surface of the drum to form about ten monolayers per revolution. The newly formed surface was then bombarded with a dilute stream of the hydrocarbon vapour (*ca.* 1/10 of a monolayer) issuing from an adjacent jet. The hydrocarbon molecules and any reaction products were trapped in the surface and subsequently covered by the next layer of NaCl which was itself bombarded with further hydrocarbon molecules. Thus a continuous interleaving spiral of product and NaCl layers was built up and the

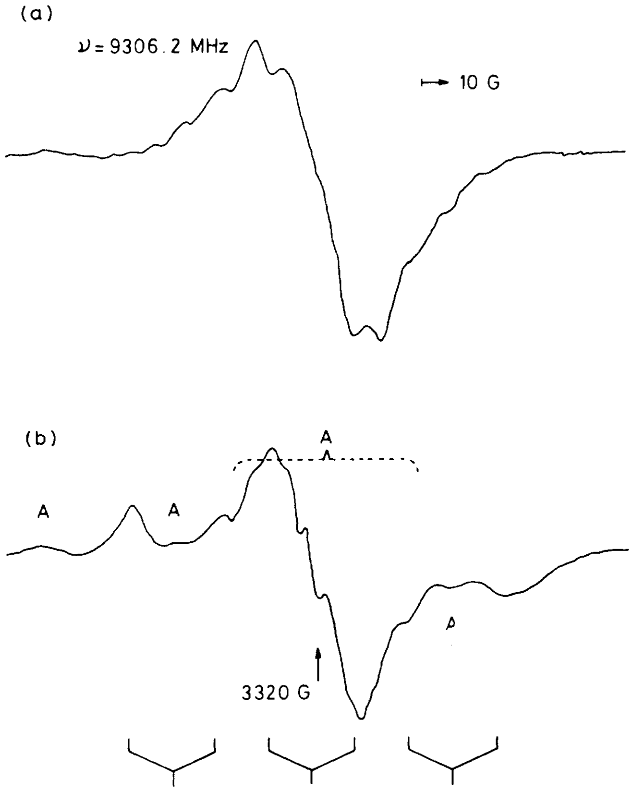

Figure 1. E.s.r. spectra at 77 K of hydrocarbon radicals formed by interaction with clean sodium chloride surfaces of (a) 2,5-dimethylhex-3-ene, and (b) cyclohexane.

deposit (*ca.* 2 mm thick after 30 min) could be transferred at 77 K and under high vacuum into sample tubes suitable for insertion into the cavity of an e.s.r. spectrometer. There are two important aspects: (i) the large surface area that was generated (*ca.* 700 m^2) by forming the spiral and (ii) since the time between the formation of NaCl surface and exposure to the hydrocarbon was $<10^{-2}$ s only 1/100 of a monolayer of background contaminant could deposit before the hydrocarbon struck the surface, *i.e.* the hydrocarbon interacted with a virtually uncontaminated surface.

The e.s.r. spectra of deposits formed when NaCl was bombarded with cyclohexane and 2,5-dimethylhex-3-ene (Figure 1) show the presence of broad anisotropic lines with hyperfine interactions (h.f.i.) typical of the expected hydrocarbon radicals together with resonances (marked A) which arise from paramagentic centres due to the NaCl deposit itself and are seen in blank experiments without hydrocarbon. The features from 2,5-dimethylhex-3-ene spaced by 14 ± 1 G† with $g = 2.0029 \pm 0.0005$ are characteristic of allylic species and can be assigned with some confidence to the allyl radical formed by β-tertiary C–H bond breakage in the alkene, although the width of the lines and the underlying NaCl features make it impossible to use intensity ratios for characterisation. The identification of the radical from cyclohexane as cyclohexyl is more equivocal because of the width of the lines, their anisotropy, and the interference from the NaCl features although, there is little doubt that the spectrum is due to an alkyl radical. The lines were shown to be due to coupling with the protons of the cyclohexane by using c-C_6D_{12} instead of c-C_6H_{12} when only an augmented central line was observed. The stick diagram in Figure 1(b) corresponds to a triplet of doublets with spacing of 46, and 30 G respectively; there is some indication of a further h.f.i. of 4 G in the central features. As in the case of cyclohexyl radicals in a variety of non-polar solids[9–12] it appears that only two of the β protons show an appreciable coupling of *ca.* 40 G with a very small coupling of *ca.* 4 G to the other β protons and a coupling of *ca.* 30 G to the single α proton. The small β h.f.i. is due to the protons in the two β C–H bonds near the nodal plane of the p-orbital while the large β h.f.i. is due to those in the two bonds nearly perpendicular to the nodal plane. The value of the α-H h.f.i. is significantly greater than that in non-ionic solids (a_α = *ca.* 20 G) and could result from a conformational distortion of the radical centre in the ionic solid. The highly anisotropic nature of the spectrum also suggests that the strong electrostatic fields are producing distortion and may confer some σ character.

There was the possibility that the radicals were formed merely by pyrolysis of the hydrocarbon on the surface as it was bombarded by hot NaCl and subjected to the latent heat of condensation of the next layer of condensing NaCl. This was discounted by interposing a jet of water vapour between the hydrocarbon and the NaCl jet positions so that the hydrocarbon molecules on the surface were covered by several layers of water before the next layer of NaCl was deposited. Hydrocarbon radicals were still formed, though the signal intensity per cm^3 was less because of dilution by the water quench layers.

It appears that the electrostatic fields at an uncontaminated NaCl surface can cause scission of C–H bonds with strengths >400 kJ mol^{-1}. The mechanism by which bond breakage occurs cannot be determined from these experiments (no e.s.r. lines due to H-atoms were observed) but probably involves charged intermediates such as RH^+ or R^+ which either react with other hydrocarbon molecules or subsequently accept electrons from the surface defects. There must be substrate surface bonding to compensate for the endothermic C–H bond breakage and allow reaction to occur at 77 K. Other ionic solids and substrates are being examined to obtain information about the mechanism.

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† 1 G = 10^{-4} T.