Dimethylcarbene Dimerisation on a Raney Nickel Surface[1]

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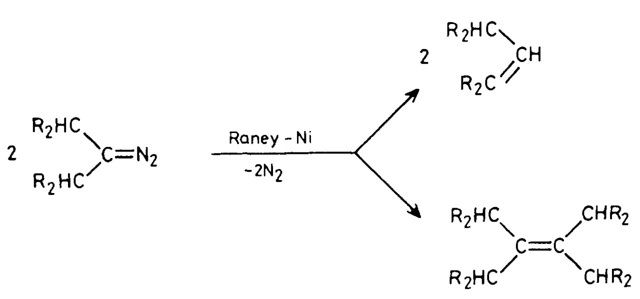
Raney nickel, a highly active heterogeneous catalyst, causes the elimination of N_2 from diazopropane quantitatively at 100 °C yielding propene and 40% of tetramethylethylene, an observation further supporting the surface methylene mechanism of the Fischer–Tropsch synthesis.

Reactions of diazomethane on Fe, Ru, Co, Ni, Pd, and Cu catalysts[1] have contributed decisively to the generally accepted methylene mechanism for the Fischer–Tropsch synthesis.[1] For our investigations, Raney nickel,[2] a highly active heterogeneous catalyst,[3] was selected. Dialkyl substituted diazomethanes containing β hydrogen atoms can react *via* two competing pathways: migration and dimerization,[4] which are both associated with the loss of N_2 (Scheme 1).

Diazopropane,[5] prepared from acetone hydrazone and anhydrous hydrazine[5] in dioxane, can be selectively evaporated at 10^{-2} mbar from the red solution thus obtained cooled to 190 K. According to the ionization energy (I.E.) patterns determined by photoelectron (P.E.) spectroscopy, continuously recorded for convenient analysis[6] in the flow system,† no traces of dioxane (I.E. 9.43 eV,[7] detection limit 2%) were found among the known[8] P.E. bands of the diazopropane vapour (Figure 1: A). In a preliminary experiment, its pyrolysis was studied in a quartz tube of 30 cm length and 1.5 cm diameter filled with a 5 cm length of quartz wool and heated using a temperature-controlled external furnace; N_2 evolution started at 373 K and was complete at 573 K, the only other product detected by P.E. spectroscopy being propene (Figure 1: B and C; N_2 black).

Raney nickel, prepared from crushed Ni–Al alloy with aqueous KOH under especially purified N_2[3] and transferred into the quartz tube excluding air, was dried (5 h), reduced with H_2 (2 h), and heated to 670 K until the characteristic ionization peak of H_2O at 12.62 eV[6] had completely disappeared. After connection of the cooling trap containing the diazopropane solution, the temperature was raised in 10 K steps. Even at room temperature, N_2 production and formation of propene were observed (Figure 1: P.E. spectrum analogous to C). In addition, the trap inserted between the heated quartz tube containing the catalyst and the P.E. spectrometer was cooled to 77 K and all condensable gases accumulated over 2 h. On fractionally evaporating the trap content the P.E. bands of tetramethylethylene (I.E.$_1$ 8.45, I.E.$_2$ 11.05 eV[8]) were also apparent, for oven temperatures above 323 K. Their intensity reached a maximum at 373 K (Figure 1: D, $Me_2C{=}CMe_2$ shaded according to the available reference spectrum[8]) and, assuming comparable ionization cross sections for the corresponding π ionizations, the band areas indicated a 3 : 1 ratio of propene to tetramethylethylene. In addition, the 'dimer' was isolated, purified by trap-to-trap distillation, and identified mass spectroscopically [*m/z* 84 (C_6H_{12}), 69 (*M* − Me), 42 (CMe_2), *etc.*].

Thus the thermal decomposition of diazopropane on quartz wool needs a temperature of 523 K for completion and yields exclusively N_2 and propene. On Raney nickel, the N_2 elimination temperature is lowered by at least 250 K, possibly owing to the Lewis acid function of active aluminium oxide centres also generated in the catalyst preparation.[2,3] At 373 K,



Scheme 1

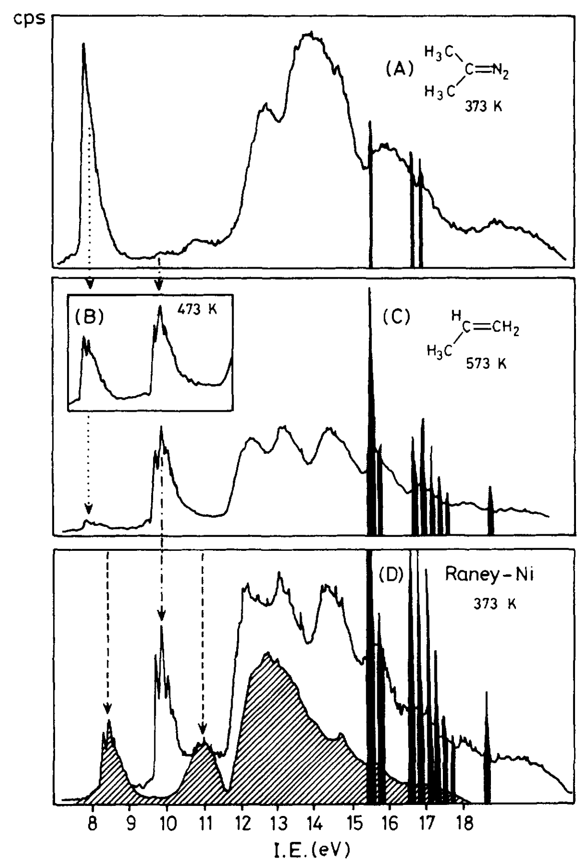
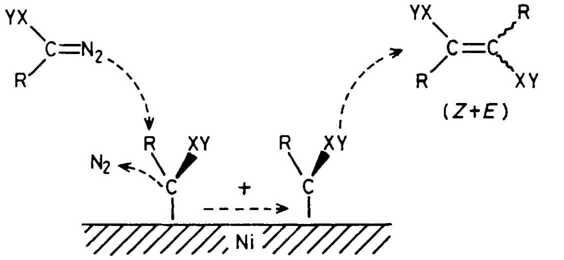


Figure 1. He I photoelectron spectra of diazopropane passing over quartz wool at (A) 373 K, (B) 473 K (insert), and (C) 573 K (N_2 black). On Raney Ni, N_2 is eliminated quantitatively at 293 K [P.E. spectrum analogous to (C); propene ionization – – · – →] and at 373 K the additional P.E. bands of tetramethylethylene (D, shaded according to reference P.E. spectrum,[9] π ionization · · ·→) reach their maximum intensity.

† The apparatus consists of the compound container connected, *via* an intermediate evacuation outlet, to a quartz tube containing the catalyst inside a temperature-controlled furnace, and being connected *via* a cooling trap to the P.E. spectrometer.



Scheme 2

ca. 40% of the formal Me_2C fragments dimerize to form tetramethylethylene, the observation of which strongly suggests the formation of dimethylcarbenes[1] as surface intermediates, which can desorb with dimerization to give the corresponding ethylene derivative (Scheme 2).

The ratio of the competing pathways on the Ni_x/AlO_n surface of Raney nickel[2] depends on the substituent stabilization of the chemisorbed carbene YX–C–R and thus on the possibility of forming more stabilized dimerization products; for example, methyl diazoacetate (YX = CO_2Me and R = H), *i.e.* containing a CO_2Me substituent which is presumably carbene-stabilizing, and having no shiftable β hydrogen, reacts under the same conditions in the same apparatus at 373 K to yield quantitatively a mixture of dimethyl maleate and fumarate.[3]

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‡ *Note added in proof:* One of the referees pointed out previous experiments by J. J. Rooney and A. Stewart mentioned in 'Catalysis', Specialist Periodical Report, ed. C. Kemball, Royal Society of Chemistry, 1977, Vo. 1, p. 277.