86. *Interaction of Olefins, Carbon Monoxide, and Steam.*

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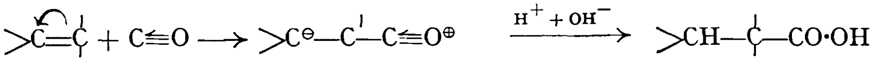
The experiments described in the two preceding papers have furnished evidence which strongly suggests that, under high pressure and in presence of acidic catalysts, olefins are capable of uniting with carbon monoxide and steam to give acids (cf. U.S.P. 1,924,762—8, 1,957,939). This hypothesis has now been confirmed with ethylene, propylene, and Δ^{β}-butylene. Passage of a mixture of the first with carbon monoxide and steam through phosphoric acid caused slow formation of propionic acid, but ethyl alcohol and ethylenic polymerides were also produced. Under 150 atm. and at 290—300°, it was found that, for every molecule of ethylene converted into acid, approximately three were hydrated and two polymerised, a position which recalls the difficulties encountered in the conversion of ethyl alcohol into propionic acid (Hardy, this vol., p. 358). Treatment of propylene and Δ^{β}-butylene at 200° and 200 atms. caused fairly rapid formation of liquid products, which contained a large proportion of acids, together with hydrocarbons. As was indicated in the collateral experiments with the alcohols (two preceding papers), propylene gave a mixture of *iso*butyric acid and homologues, and Δ^{β}-butylene produced pivalic, methylethylacetic, and higher acids.

Formation of acids from olefins, steam, and carbon monoxide must be due primarily to activation of the olefin molecule, which is then able to unite with carbon monoxide, reaction being completed by addition of the elements of water :



$$>C{=}C< + C{\equiv}O \longrightarrow >C^{\ominus}{-}C{-}C{\equiv}O^{\oplus} \xrightarrow{H^{+} + OH^{-}} >CH{-}C{-}CO{\cdot}OH$$

When phosphoric acid is used as catalyst, activation doubtless occurs by formation and subsequent decomposition of alkyl phosphates.

EXPERIMENTAL.

Apparatus.—The high-pressure circulatory apparatus (Hardy, J., 1934, 1339) was employed, but for the experiments with propylene and Δ^{β}-butylene the force-pump was disconnected from the vaporiser. The latter contained an initial charge of water, and the liquid hydrocarbons were withdrawn from inverted cylinders by means of the force-pump and delivered into the apparatus at a point in front of the first preheater.

Materials.—Propylene was prepared from *iso*propyl alcohol (Senderens, *Compt. rend.*, 1910, **151**, 394 ; *Bull. Soc. chim.*, 1911, **9**, 373) obtained by catalytic hydrogenation of acetone. By means of a Geryk pump it was compressed into a cylinder cooled to − 20°. Δ^{β}-Butylene was obtained from *n*-butyl alcohol and 60% sulphuric acid (Young and Lucas, *J. Amer. Chem. Soc.*, 1930, **52**, 1964) and was liquefied by cooling to − 20°.

Ethylene, Carbon Monoxide, and Steam.—A mixture of ethylene (1 vol.) and carbon monoxide (4 vols.) under a pressure of 150 atm. was circulated at a rate of 40 l. of compressed gas per hour through phosphoric acid (350 g. of 87%) at 290—300°. The product (500 g.) contained an upper layer (16·5 g.) of high-boiling hydrocarbons, and a lower, aqueous layer (acidity, 0·5*N*). After neutralisation with sodium hydroxide solution, the latter gave an alcoholic distillate equivalent to 37 g. of ethyl alcohol, and a residual solution of sodium salts, which was concentrated and treated with *p*-phenylphenacyl bromide; *p*-phenylphenacyl propionate (m. p. 95—97°; mixed m. p. 97—99°) was obtained.

Propylene, Carbon Monoxide, and Steam.—Carbon monoxide under 200 atms. was led (40 l. of compressed gas per hour) through phosphoric acid (700 g. of 87%) at 200°, and, the water-vaporiser being maintained at 100°, propylene (850 g.) was regularly injected during 6 hours. The product, which consisted of 546 g. of upper layer (free acid,* 41·5; total acid,* 50·8%) and 284 g. of lower layer (free acid,* 6·2%), was boiled under reflux with sodium hydroxide solution (110 g. in 250 c.c.) for 2 hours, and was then distilled until only water was passing over. Repeated washing of the upper layer of distillate with water gave 88·4 g. of hydrocarbons, etc., and distillation of the washings gave a small amount of aqueous *iso*propyl alcohol (equivalent to 3 g. of alcohol). Non-volatile hydrocarbons, etc. (61·3 g.), were separated from the residue which, after concentration, was strongly acidified with concentrated hydrochloric acid. The liberated acids were extracted with benzene, dried by the azeotropic method, and distilled: $< 150°$ (1·7 g.), 150—159° (105·0 g.), 159—175° (14·1 g.), residue (173 g.). A portion of acid, b. p. 154—155°, gave an anilide, m. p. and mixed m. p. with *iso*butyranilide 102·5—103°. The absence of *n*-butyric acid was shown by converting a portion of acid of b. p. 163—164° into its anilide, which formed needles, m. p. 100—101·5° (*n*-butyranilide crystallises in rhombs, m. p. 94°). Admixture with *iso*butyranilide depressed the m. p. to 98—98·5°.

Δ^{β}-Butylene, Carbon Monoxide, and Steam.—Under conditions described in the foregoing experiment, Δ^{β}-butylene (640 g.) gave a product consisting of upper layer (110 g.; free acid,† 66·4%) and lower layer (528 g.; free acid,† 7·0%), from which hydrocarbons, etc. (10·6 g.), and acids were similarly isolated. The latter were distilled as follows: 160—168° (32·5 g.), 168—190° (23·1 g.), and residue (24·2 g.), and the two fractions of the distillate were separately converted into methyl esters, which were fractionally distilled through a 2′ 6″ Dufton column fitted with a dephlegmator. The combined fractions were as follows: 99—104° (32·8%), 104—109·5° (26·5%), 109·5—114° (13·5%), 114—118° (22·6%), residue (4·6%). Fraction 1 consisted of methyl pivalate, and on treatment with anilinomagnesium bromide (Hardy, this vol., p. 398) gave pivalanilide, m. p. 125—126° and mixed m. p. 127—128°. Fraction 4 contained methyl methylethylacetate, and in like manner gave methylethylacetanilide, m. p. and mixed m. p. 107—108°.

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* Calculated on the assumption that the molecular weight of acid is 88.

† Calculated on the assumption that the molecular weight is 102.