COMMUNICATIONS TO THE EDITOR

OXIDATIVE COUPLING OF BUTANES TO OCTANES

Sir:

The simplest method of converting low molecular weight paraffins into higher molecular ones would be a one-step synthesis consisting in the oxidative coupling of two paraffin molecules by means of molecular oxygen, in line with the over-all equation

$$2C_nH_{2n+2} + {}^1/_2O_2 \longrightarrow C_{2n}H_{4n+2} + H_2O \qquad (1)$$

Unfortunately, all known methods of oxidation of paraffins lead, at best,[1] to oxidation products of the original paraffin containing the same number of carbon atoms. It was anticipated, however, that if paraffin molecules are pressed so tight that they cannot orient themselves and are forced to react with deficient amounts of oxygen in such close proximity to each other that successive oxidation of the same molecule would become highly improbable, *simply because of restrictions of geometry*, oxidative coupling of two close-lying paraffin molecules might occur. Under ideal coupling conditions the oxygen is forced to react with hydrogen atoms in its immediate vicinity and equal reactivities for primary and tertiary C–H-bonds are to be expected. Thus *isobutane* would couple to yield only: 2,5-dimethylhexane, 2,2,4-trimethylpentane and 2,2,3,3-tetramethylbutane, while *n-butane* would give only: *n*-octane, 3-methylheptane and 3,4-dimethylhexane. *Iso-* and *n-butane* were chosen for our experiments because any likely reaction products can be easily analyzed; furthermore they can be readily compressed to desired loading densities. It was assumed that favorable coupling conditions might prevail at pressures over 20,000 p.s.i. and at 300–350°, *i.e.*, below their thermal cracking range.

Isobutane (99.5+%) containing 4.4 mole % dissolved O_2, was heated in a 30-cc. Aminco Superpressure reactor at 325 ± 5° and at 23,000 p.s.i. pressure for 20–24 hours. It was found that over 80% of the O_2 reacted, forming only traces of CO_2 and CO; H_2O was formed in amounts corresponding to one-fourth of the O_2 consumed. Sixteen identical experiments yielded 9.0 g. of reaction products (b.p. > isobutane). They were divided into: (a) normal oxidation products of isobutane = 75 vol. % and (b) coupling products = 25 vol. %.

(a) consisted of $\simeq$75 vol. % *t*-butanol and 25 vol. % of its degradation products, acetone and methanol.

(b) consisted of octanes, after removal of olefin traces. Microanalysis gave: 81.55% C, 15.17% H, or $CH_{2.22}$ (calcd. for C_8H_{18} = 2.25, for C_8H_{16} = 2.00). Infrared and mass spectra identified the following in vol. % of (b) *2,5-dimethylhexane* 40%, *2,2,4-trimethylpentane* 38%, *2,2-dimethylhexane* 8%, *2,2,3,3-tetramethylbutane present*, other octanes and octanes—possible traces. No masses above octanes were observed in the spectrum.

Identical conditions were used with *n*-butane; 25 vol. % of the product analyzed as follows: *n-octane* 10%, *3-methylheptane* 40–50%, *3,4-dimethylhexane* 30%; other paraffins and possibly olefins 10–20%.

Thus with each butane the three expected octanes were produced. They were also the *only* octanes observed, with the exception of 2,2-dimethylhexane. This abnormal octane is perhaps due to isomerization "*in statu nascendi*." The amount of water found is also in agreement with equation 1.

The data presented indicate that under the conditions given the usual oxidation paths, although not eliminated, are sufficiently restricted so that the coupling reaction can be readily observed. No attempt to discuss possible mechanisms of this reaction will be made at this time.

The effect of highly restricted geometrical conditions, due to high pressure, on reaction paths, is, of course, not limited to paraffins and can be expected to yield interesting results with other types of compounds.

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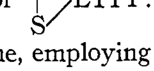
[1] Usually complete breakdown to CO, CO_2 and H_2O takes place.

MECHANISM OF ENZYMATIC OXIDATIVE DECARBOXYLATION OF PYRUVATE

Sir:

The generation of active acetate (acetyl CoA[1]) from pyruvate by purified pyruvate oxidase preparations from bacterial[3] and animal[4,5] sources has been formulated as shown in reaction 1. TPN^+ will not replace DPN^+ in this reaction.[4]

$$\text{Pyruvate} + DPN^+ + CoA \longrightarrow \text{Acetyl CoA} + DPNH + CO_2 + H^+ \qquad (1)$$

Studies[6] with soluble pyruvate apoöxidase preparations from an *Escherichia coli* mutant which cannot synthesize LTPP[7] reveal that reaction 1 does not proceed in the absence of  $\begin{smallmatrix}S\\|\\S\end{smallmatrix}\!>\overline{L}TPP$. An analysis of the role of this coenzyme, employing

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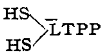
[1] The following abbreviations are used: CoA or Co$\overline{A}$-SH = coenzyme A; DPN^+, DPNH and TPN^+, TPNH = oxidized and reduced diphospho- and triphosphopyridine nucleotides, respectively;  $\begin{smallmatrix}S\\|\\S\end{smallmatrix}\!>\overline{L}TPP$ and  $\begin{smallmatrix}HS\\HS\end{smallmatrix}\!>\overline{L}TPP$ = oxidized and reduced lipothiamide pyrophosphate (LTPP),[2] respectively; TPP = thiamine pyrophosphate.

[2] (a) L. J. Reed and B. G. DeBusk, THIS JOURNAL, **74**, 3964 (1952); (b) *J. Biol. Chem.*, **199**, 881 (1952).

[3] S. Korkes, *et al.*, *ibid.*, **193**, 721 (1951).

[4] J. W. Littlefield and D. R. Sanadi, *ibid.*, **199**, 65 (1952).

[5] R. S. Schweet and K. Cheslock, *ibid.*, **199**, 749 (1952).

[6] L. J. Reed and B. G. DeBusk, unpublished results.

[7] L. J. Reed and B. G. DeBusk, THIS JOURNAL, **74**, 4727 (1952).