The present radical-trap study of the reactions of TNM with α-nitrocarbanions has led to the detection and identification of short-lived $R_1R_2\overset{\cdot}{CNO_2}$ and NO$_2$ radicals such as could be expected to result from single-electron transfer processes [cf. equations (1), (2)]. The formation of these radicals speaks in support of a single-electron mechanism for these reactions, other types of mechanism appearing to be less probable.

**CONCLUSIONS**

Radical-trap methods have been used to show the formation of short-lived $R_1R_2\overset{\cdot}{CNO_2}$ and NO$_2$ radicals in the reactions of tetranitromethane with α-nitrocarbanions $R_1B_2^\cdot\overset{\cdot}{CNO_2}$ in aprotic solvating solvents.

**LITERATURE CITED**

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In a kinetic isotope study of the mechanism of C$_5$-dehydrocyclization of paraffin hydrocarbons on aluminoplatinum catalysts.

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The mechanism of hydrocarbon C$_5$-dehydrocyclization (C$_5$-DHC) on various types of Pt catalysts has been studied in considerable detail [1-6]. There is, however, no general agreement as to the role played by unsaturated hydrocarbons in these reactions [1, 2].

Since both alkanes and olefins undergo C$_5$-DHC on Pt/Al$_2$O$_3$ (0.6\% Pt) catalysts, it has been postulated that five-membered ring formation can proceed either directly by alkane dehydrocyclization or indirectly by formation of an intermediate olefin with the same type of carbon skeleton. In order to obtain more detailed information on the role of olefin intermediates in C$_5$-DHC on Pt/Al$_2$O$_3$ catalysts, we have carried out kinetic isotope (KI) studies on the reactions of 2-methylpentane (2-MP) and methylcyclopentane (MCP) [7], working in pulsed and flow systems.
Pulsed studies of the reactions of binary mixtures of 2-MP and 2-methyl-2-pentene (1-14C) (2-MP-2) on two different types of Pt/A1203 catalysts (A and B) * at 370°C showed the molar radioactivity of the product MCP to be higher than that of the olefin (Fig. 1). This indicates, according to [7], that olefins are actually intermediates in DHC reactions carried out under these conditions. On this basis the general scheme for MCP formation would have the form

\[
\begin{align*}
2-\text{Methylpentane} & \rightarrow 2-\text{Methylpentene} \\
W_2 & \rightarrow \text{MCP} \\
W_3 & \rightarrow \text{Benzene}
\end{align*}
\]

\(W_2\) and \(W_3\) representing the respective rates of MCP formation from alkane and olefin. Values of \(W_2\) and \(W_3\) cannot be determined individually since the product MCP undergoes dehydroisomerization in benzene. A value of the \(\frac{W_2}{W_2 + W_3}\) ratio can be obtained, however, if the conditions are such that the ratio of 2-MP and 2-MP-2 concentrations remains essentially constant during the time of contact with the catalyst, calculations then following through the equation [7]

\[
\gamma = \frac{4}{\tau} \left( X \int_0^\tau a \, dt + (1 - X) \int_0^\tau \beta \, dt \right)
\]

in which \(\alpha\), \(\beta\), and \(\gamma\) are the respective molar radioactivities of 2-MP, 2-MP-2, and MCP, \(\tau\) is the contact time, and \(X = \frac{W_2}{W_2 + W_3}\).

Methylcyclopentane molar radioactivities were calculated for various values of \(X\) and the results obtained compared with the measured values. Values of \(\int_0^\tau a \, dt\) and \(\int_0^\tau \beta \, dt\) were obtained by graphical integration. The indication was that \(X = 0.3\) for the A-type catalyst and \(X = 0.1\) for the B-type catalyst (Fig. 2). Thus, the olefin was the source of the major portion of the MCP formed in reaction under the conditions in question here (370°C, He). The data of Table 1 indicate that there is a relation between the acidity of the catalyst and the ability of the catalyst to promote isomerization [9]. In fact, dehydroisomerization could be suppressed by introducing an alkali metal to reduce the acidity of the Pt/A1203 catalyst.

The fact that MCP was not formed in experiments carried out in He on a catalyst which had not been given a preliminary treatment with H₂ confirmed the claim of [3, 4] that H₂ must be present in systems which are to undergo C₅-DHC reactions.

Experiments in the flow system were carried out at 330 and 400°C, using an A-type catalyst and working with ternary mixtures containing 4.4 - 10% 2-MP and 2-MP-2 (1-14C) and 0.5% unlabeled MCP. If the olefin was indeed a precursor of the MCP, KI considerations would require the MCP radioactivity curve to pass through a maximum at the point of intersection with the olefin radioactivity curve.

Since the MCP molar radioactivity curve of Fig. 3 lies below the molar radioactivity curve for the olefin, part of the product MCP must have come from the radioactive olefin and part from the original alkane. Thus, alkane C₅-DHC proceeds through parallel-successive reactions on Pt/A1203 catalysts. Comparison showed that there was little difference in the molar radioactivities of MCP and olefin obtained with extended contact times at 400°C, but the same was not true at 330°C. Here it would be reasonable to assume that most of the MCP is formed through the intermediate olefin.

Thus, the data obtained here suggest that C₅-DHC reactions can proceed either through an olefin intermediate or through direct cyclization of the alkane on Pt/A1203 (0.6% Pt) catalysts, the relative significance of the two reaction paths varying with the temperature and contact time. Our data support the claim of [4] that the olefins are precursors of the cyclopentanes, thus confirming the reality of the first of the two reaction paths.

*The catalysts were prepared by the method of [8], the carrier being treated with a NaNO₃ solution in the case of the A modification, and with an equivalent amount of a HNO₃ solution in the case of the B modification [8].