

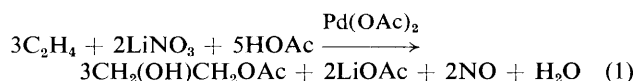
The Mechanism of Formation of Ethylene Glycol Monoacetate from Ethylene in the System $\text{MeCO}_2\text{H} + \text{LiNO}_3 + \text{Pd}(\text{OAc})_2$

Nina I. Kuznetsova, Vladimir A. Likholobov, Martin A. Fedotov, and Yurii I. Yermakov*

Institute of Catalysis, Novosibirsk 630090, USSR

A ^{17}O n.m.r. study has shown that formation of ethylene glycol monoacetate from ethylene in acetic acid solution containing LiNO_3 and $\text{Pd}(\text{OAc})_2$ is accompanied by oxygen atom transfer from the oxidant to the carbonyl group of the product.

Oxidation of ethylene by lithium nitrate in acetic acid containing $\text{Pd}(\text{OAc})_2$ proceeds with the formation of ethylene glycol monoacetate (EGMA) [equation (1)].¹



Although little is known about the mechanism of this interaction, it is quite evident that it differs from the mechanism of ethylene oxidation by Pd^{II} salts to carbonyl compounds.²

We have studied the oxygen atom transfer from the nitrate anion and acetic acid to ethylene during the formation of EGMA. The distribution of ^{17}O in the reaction products was determined using reagents enriched with ^{17}O .

The oxidation of ethylene was performed at 50 °C under atmospheric pressure of ethylene [$\text{Pd}(\text{OAc})_2$ 0.02 mol l^{-1} , LiNO_3 0.7 mol l^{-1}]. In one hour 30 mol of C_2H_4 per mol of Pd^{II} were oxidized; the main product (90%) was EGMA. EGMA for the ^{17}O n.m.r. study was obtained (i) from reagents with their natural content of ^{17}O , according to equation (1), (ii) using lithium nitrate with a ^{17}O content 20 times higher than natural, or (iii) using MeCO_2H enriched 5-fold with ^{17}O .

^{17}O N.m.r. spectra were recorded at 40.7 MHz using a Bruker FT spectrometer CXP-300 at 20 °C. The 90° pulse width was 10 μs , the number of accumulations was 10000–20000 with a frequency of 50 Hz. 20–50 vol. % solutions of EGMA in CCl_4 were used for the measurements.

The ^{17}O n.m.r. spectrum of EGMA consists of three lines ascribed to three non-equivalent O-atoms with the intensity ratio 1:1:1. The ^{17}O n.m.r. spectrum of the non-enriched EGMA [$\text{CH}_2(\text{OH})\text{CH}_2\text{O}(\text{Me})\text{C}=\text{O}$] [Figure 1(a)] exhibits three lines at δ 364 (C=O), 162 (CH_2O), and -4 p.p.m. [$\text{CH}_2(\text{OH})$] with respect to external D_2O . The assignment of the lines is based on a diagram of chemical shifts for ^{17}O .³ As is seen from the spectrum of the sample prepared from enriched $\text{LiN}^{17}\text{O}_3$ [Figure 1(b)] the oxygen carbonyl atom in EGMA is derived from lithium nitrate, whilst the other oxygen atoms are derived from acetic acid. This was confirmed by the spectrum of EGMA obtained from the ^{17}O -enriched acetic acid and lithium nitrate [Figure 1(c)] Hence, the formation of EGMA may be described by equation (2).



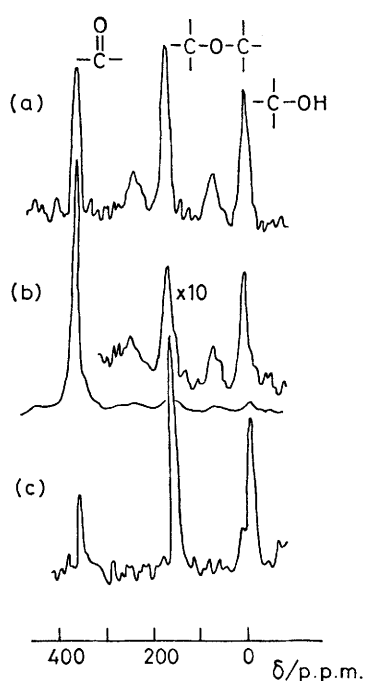
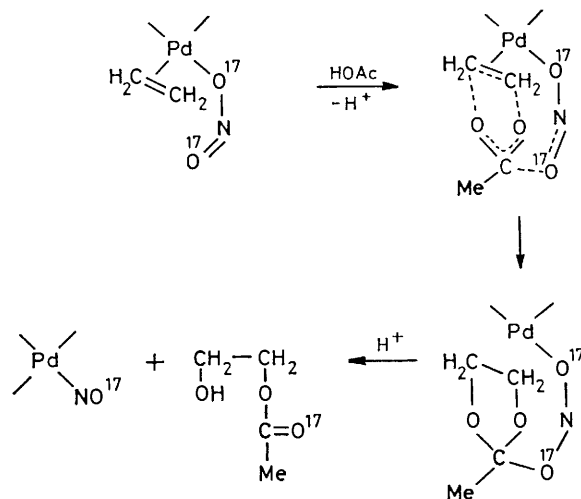


Figure 1. ^{17}O N.m.r. spectra of EGMA obtained (a) from reagents with a natural content of ^{17}O ; (b) using LiNO_3 enriched with ^{17}O ; (c) using MeCO_2H enriched with ^{17}O .

It was found⁴ that, in the formation of EGMA, ethylene interacts with nitrite complexes of palladium, formed at the initial stage of the reduction, but not with the nitrate itself. During the oxidation of ethylene the nitrite complex was reduced with ethylene to produce a nitroso-complex of palladium(II) which was then isolated from the solution.⁵ The oxygen atom is transferred from the NO_2^- anion during the reduction. In principle, oxygen transfer to the olefin may be due to direct interaction of the olefin with the oxidant. This has been observed for olefin oxidation to aldehydes and ketones by nitrite complexes of Co^{III} ⁶ and Pd^{II} .⁷ In the latter case oxygen transfer from the NO_2^- anion to the olefin was



Scheme 1

detected using isotope methods. In the reaction under study 'nitrite' oxygen is found to be in the carbonyl position of the EGMA molecule. As an explanation of this surprising result we propose the mechanism for EGMA formation shown in Scheme 1.

Received, 19th April 1982; Com. 429

References

- 1 M. Tamura and T. Yasui, *Chem. Commun.*, 1968, 1209.
- 2 P. M. Henry, 'Palladium Catalysed Oxidation of Hydrocarbons,' Dordrecht, Boston, London, 1980.
- 3 W. G. Klemperer, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 246.
- 4 N. I. Kuznetsova, A. F. Danilyuk, V. A. Likhonobov, and Yu. I. Yermakov, *React. Kinet. Catal. Lett.*, 1979, **12**, 235.
- 5 N. V. Podberezovskaya, V. V. Bakakin, N. I. Kuznetsova, A. F. Danilyuk, and V. A. Likhonobov, *Dokl. Akad. Nauk SSSR*, 1981, **256**, 870.
- 6 B. S. Tovrog, F. Mares, and S. E. Diamond, *J. Am. Chem. Soc.*, 1980, **102**, 6616.
- 7 M. A. Andrews and K. P. Kelly, *J. Am. Chem. Soc.*, 1981, **103**, 2894.