BRIEF COMMUNICATIONS

MECHANISM FOR FORMATION OF ETHYLENE GLYCOL MONOACETATE FROM ETHYLENE IN ACETIC ACID SOLUTION CONTAINING LITHIUM NITRATE AND PALLADIUM ACETATE

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Ethylene is catalytically oxidized by lithium nitrate in acetic acid solution containing palladium acetate to give ethylene glycol monoacetate (EGMA) [1]:

$$3C_2H_4 + 2LiNO_3 + 5HOAc \xrightarrow{Pd(OAc)_2} 3CH_2(OH)CH_2OAc + 2LiOAc + 2NO + H_2O$$

The mechanism of this reaction was studied inadequately [2], and it is only clear that it differs from the known mechanism for the oxidation of ethylene by Pd(II) salts.

The processes for the transfer of oxygen from nitrate anion and acetic acid to ethylene with the formation of EGMA were studied in the present paper. For the purpose we used reactants enriched with the ^{17}O isotope, and followed its distribution in the reaction products employing ^{17}O NMR.

The oxidation of ethylene was run at 50°C and atmospheric ethylene pressure for 1 h ($[Pd(OAc)_2] = 0.02$, $[LiNO_3] = 0.7$ mole/liter. The reaction products, which when analyzed were 90% EGMA, were isolated by extracting the neutralized solution with ether and subsequent removal of the ether by distillation. Three methods were used to obtain the EGMA for the ^{17}O NMR study. In the first case the EGMA was obtained by reaction (1) from reactants with the natural amount of ^{17}O. In the second case, instead of the usual $LiNO_3$, we used a lithium nitrate that was enriched 20 times in the ^{17}O isotope, and in the third case we used acetic acid that was enriched 5 times in the ^{17}O isotope.

The ^{17}O NMR spectra were taken on a Fourier SXP-300 NMR spectrometer at 20° and a frequency of 40.7 MHz. The duration of the 90° pulse was 10 μsec, the frequency of the pulse repetitions was 50 Hz, and the number of accumulations was 10,000-20,000. The recordings were made using CCl_4 solutions of the EGMA samples (20-50 vol.%).

The ^{17}O NMR spectrum of EGMA should have three lines, corresponding to three nonequivalent O atoms, with an intensity ratio of 1:1:1. In the spectrum of the unenriched EGMA $CH_2(\overset{c}{O}H)CH_2\overset{b}{O}(CH_3)C=\overset{a}{O}$ (Fig. 1, spectrum 1) the lines at 364 (a), 162 (b), and −4 ppm (c) relative to deuterium oxide belong to EGMA. The assignment of the spectrum was made on the basis of the diagram of the ^{17}O chemical shifts [3] and the NMR spectra of analogous oxygen atoms in other organic compounds. The spectrum of the sample obtained from enriched $LiN^{17}O$, (see Fig. 1, spectrum 2) shows that the carbonyl oxygen atom migrates to the EGMA from lithium nitrate, whereas the other oxygen atoms migrate to the EGMA from acetic acid. Spectrum 3 of the EGMA obtained using ^{17}O enriched acetic acid and ordinary $LiNO_3$ confirms these migration routes. As a result, the process for forming EGMA can be depicted by the following equation:

$$3C_2H_4 + 2LiNO_3^* + 5CH_3COOH \rightarrow 3CH_2(OH)CH_2O(CH_3)C{=}O^* + 2LiOCOCH_3 + H_2O + 2NO^*$$

In [4] it was established that in the formation of EGMA the ethylene does not react with the nitrate itself, but rather with the Pd nitrate complexes that are formed in the initial period of reaction. The Pd nitroso complex [5] was isolated from solution during the oxidation of the ethylene, which complex is formed by the ethylene reduction of the nitrite complex. As our obtained data show, the transfer of an oxygen atom from the NO_2^- group occurs during such reduction. The transfer of oxygen to the olefin without involving exchange processes can be

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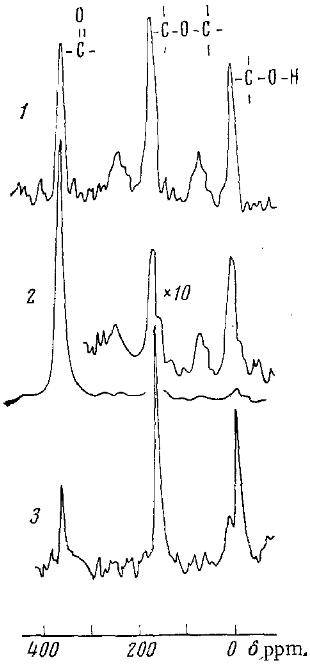
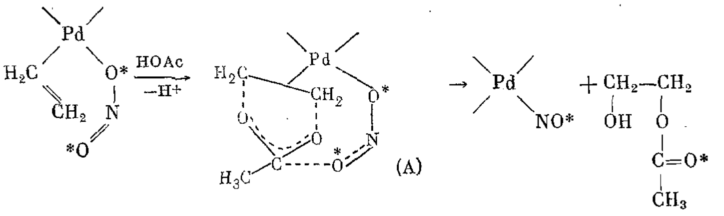
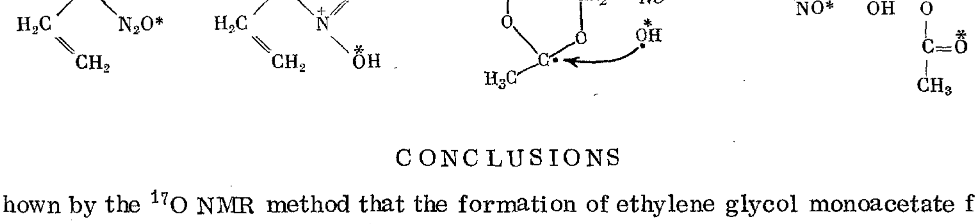


Fig. 1. ^{17}O NMR spectra of EGMA: 1) unenriched product; 2) product obtained using enriched $LiNO_3$; 3) product obtained using enriched acetic acid.

explained only by the direct reaction of the olefin with the oxidizing agent. Such a reaction is postulated, for example, in the case of oxidizing olefins to aldehydes and ketones by the nitrite complexes of Co(III) [6] and Pd(II) [7], whereas in the latter case the transfer of oxygen from the NO_2^- anion to the olefin was detected by isotopic methods. It is interesting that in our studied reaction the "nitrite" oxygen proves to be in the carbonyl position of the EGMA molecule. Consequently, we believe that the formation of EGMA can proceed with the involvement of intermediate (A), in which the NO_2^- group reacts simultaneously with both ethylene and acetic acid, which assures the transition of oxygen to the carbonyl group of EGMA:



It is not excluded that the transformation of the intermediate complex containing the olefin and the NO_2^- group proceeds by another path: via the oxidation of Pd(II) by nitrite anion and subsequent transfer of an electron from the olefin to Pd(III) to give the cation-radical. This type of reaction for the oxidation of olefins was observed in the presence of



CONCLUSIONS

It was shown by the ^{17}O NMR method that the formation of ethylene glycol monoacetate from ethylene in AcOH solution containing $LiNO_3$ and $Pd(OAc)_2$ is accompanied by the transfer of an oxygen atom from the oxidizing agent to the carbonyl group of the product.

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ELECTRICAL PROPERTIES, VIBRATIONAL SPECTRA, AND CONFORMATION OF N,N-DI(CHLOROMETHYL)AMIDES

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The steric structure of molecules with two geminal axes of internal rotation has been repeatedly studied from the standpoint of the interaction of nonregular groups [1]. The conformations of the Hal–C–N–CHal groupings are of special interest since, besides the usual factors, the rotation around the C–N bonds is affected by the $n-\sigma^*$ interaction between the unshared electron pair of the nitrogen atom and the antibonding orbitals of the C–Hal bonds. Such interaction stabilizes the orthogonal orientation of the C–N–C and N–C–Hal planes [2]. We examined the steric structure of some N,N-di(chloromethyl)amides $RCON(CH_2Cl)_2$, where R = H (I), CH_3 (II), C_6H_5 (III), employing the methods of dipole moments (DM), Kerr effect (KC), IR, and Raman spectroscopy. The IR spectra of (I) and (II) in both the liquid and crystalline state, and also in CCl_4 solutions of variable concentration, lack essential differences. This points to the realization of only one conformation in all cases.

The structure of the studied compounds is determined by the angles of rotations $\varphi_{1,2}$ around the two N–C bonds (subscript 1 refers to the bond in the cis position to the carbonyl). When $\varphi_1 = \varphi_2$, the Cl atoms are located in different directions from the CNC plane, and the conformation with a trans orientation of the Cl–C–N–C–Cl chain is taken as the reference point. The structure of the conformer was established by comparing the experimentally determined DM and KC (Table 1) and those calculated for different values of φ, while in the case of (III) there is still another axis of internal rotation $C_{sp2}-C_{sp2}$, and consequently only the polarity of the molecule was discussed, which is not affected by the rotation of the phenyl radical. Following the usual concepts on the conformations of 1,3-disubstituted derivatives, one should examine the staggered conformations of the Cl–C–N–C–Cl chain: tt ($\varphi_1 = \varphi_2 = 0$), gg ($\varphi_1 = \varphi_2 = 120°$), tg ($\varphi_1 = 0$, $\varphi_2 = 120°$), gt ($\varphi_1 = 120°$, $\varphi_2 = 0$); the gg' structure ($\varphi_1 = 120°$, $\varphi_2 = -120°$), with a 1,3- parallel interaction, can be excluded from the discussion. Taking into account the conformational manifestation of the $n-\sigma^*$ interaction, we calculated the DM and KC of the molecule with a continuous change of the angles $\varphi_1 = \varphi_2$, i.e., with a local symmetry of the C_2 group. As in [3], the CNC and NCCl valence angles were respectively taken equal to 120 and 110°. The additive parameters of the bonds and groups of atoms are given in [2, 3]. The calculation results are given in Table 2. Either symmetrical confor-

TABLE 1. Polarity and Polarizability of Studied Compounds

Compound	$\frac{\Delta\varepsilon}{\Delta w_2}$	$\frac{\Delta n}{n_1\Delta w_2}$	$\frac{\Delta d}{d_1\Delta w_2}$	$\frac{\Delta B}{B_1\Delta w_2}$	μ, D	$_mK\cdot10^{12}$, esu
(I)	15,667	0,098	0,186	59,006	3,34	56
(II)	10,000	0,048	0,205	25,160	2,79	23
(III)	5,620	0,074	–	—	3,07	–

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