

FORMATION OF ACETIC ANHYDRIDE BY CARBONYLATION OF
METHYL ACETATE

V. A. Mamyán, S. D. Sominskii, S. D. Pirozhkov,
V. L. Barsegyan, V. D. Vardanyan, and A. L. Lapidus

UDC 542.91:547.292-312

Acetic anhydride (AA) is obtained by pyrolysis of acetic acid, oxidation of acetaldehyde, or thermal decomposition of ethylidene diacetate [1]. In prospect is the production of AA by carbonylation of methyl acetate (MA) in the presence of compounds of Group VIII metals mixed with $\text{Cr}(\text{CO})_6$, $\text{Co}(\text{MeCOO})_2$, PPh_3 , MeI , etc. [2-5].

The present work is devoted to studying the carbonylation reaction of MA with the formation of AA, and also to an elucidation of the mechanism of this reaction in the presence of a catalytic system including RhCl_3 , Zn acetate, and MeI .

EXPERIMENTAL

Carbonylation of MA was conducted in a 0.15-liter autoclave made of stainless steel. MA (pure grade) was first purified, dried with CaCl_2 , and distilled; MeI was of chemically pure grade.

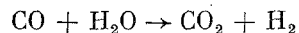
Into a 0.1-liter glass ampul was added 0.1 g of the chloride hydrate of $\text{Rh}(\text{III})$, $\text{Ru}(\text{III})$, or $\text{Pd}(\text{II})$, 0-3 g $\text{Zn}(\text{OAc})_2$, 15 ml (0.13 mole) MA, and 0-10 ml MeI . The ampul was placed in the autoclave, CO was flushed through twice, and then fed in to a pressure of 100 atm. On rotating the autoclave (90 rpm) the heating was initiated and the temperature was increased to the working temperature (100-230°C). Carbonylation of MA was also conducted using $\text{CO}:\text{H}_2$ mixtures with composition from 1:4 to 3:1.

The reaction mixture was analyzed on an LKhM-8 MD chromatograph (steel column, length 2 m, $d = 3$ mm, 15% polymethylsiloxane on Chromaton P-AW, 120-140 mesh) at 90°C. The temperature of the evaporator was 150°C. For analysis of the reaction products, including deuterated products, a Specord-IR infrared spectrometer in the region 1000-4000 cm^{-1} and a Varian CH-16 mass spectrometer were used. Elemental analysis was also employed.

DISCUSSION OF RESULTS

The results obtained (Table 1) show that the metal halides studied can be arranged in order of activity and selectivity: $\text{RhCl}_3 > \text{RuCl}_3 > \text{PdCl}_2$. Small quantities (0.2-3.0%) of acetaldehyde, butyraldehyde, acetic acid, and acetone are found in the reaction products.

By increasing the duration from 1 to 2 and then to 3 h the conversion of MA changes from 87.6 to 93.8 and 84.5%, respectively. The optimum conversion of MA (93.8%) and the maximum yield of AA are observed for a reaction time of 2 h. For a reaction time of 3 h, up to 15% acetaldehyde and 0.2% EDA are contained in the products. Acetaldehyde is formed by hydrogenation of initial MA and generated EDA with hydrogen obtained by the water gas reaction:



With an increase in H_2 content in the initial gas mixture (molar ratio $\text{CO}:\text{H}_2$ from 3:1 to 1:4) the yield of AA decreases from 88.4 to 28.5%, while the yield of acetaldehyde increases from 0.8 to 3.0%, and of acetic acid from 0.6 to 3.5%. The data of Table 2 show that if a mixture of CO and H_2 with composition 1:1 and 1:2, obtained usually by conversion of natural gas or gasification of coals, is used the conversion of MA and the yield of AA are quite high.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 10, pp. 2265-2268, October, 1985. Original article submitted June 5, 1984.

TABLE 1. Effect of Nature of Metal Halide on Its Activity in the Carbonylation Reaction of Methyl Acetate*

Metal halide	Conversion of MA		Content in mixture, %				
	%	moles MA/ moles MCl _x	AA	acetaldehyde	butyraldehyde	acetic acid	acetone
RhCl ₃ ·3H ₂ O	93,8	1360	92,0	2,6	0,3	3,5	0,9
RuCl ₃ ·4H ₂ O	50,2	183	88,6	0,6	0,2	2,7	1,3
PdCl ₂ ·2H ₂ O	45,3	164	65,6	2,8	3,2	3,0	0,6

*Fed in: 0.1 g MCl_x·yH₂O, 3 g Zn(OAc)₂, 15 ml (0.13 mole) MA, 5 ml (0.08 mole) MeI. Reaction conditions: 200°C, pCO = 100 atm, CO:H₂ = 1, τ = 2 h.

TAP 2. Dependence of Yield of Acetic Anhydride on the R, CO:H₂*

Molar ratio CO:H ₂	Conversion of MA, %	Content in mixture, %				
		AA	acetaldehyde	butyraldehyde	acetic acid	acetone
1:0	95,2	97,8	0,5	—	1,7	—
3:1	91,7	96,4	0,9	0,2	1,6	0,7
2:1	91,4	94,8	2,1	0,4	1,3	1,3
1:1	93,8	92,0	2,6	0,3	0,9	3,5
1:2	92,6	87,5	4,2	1,0	0,5	6,8
1:4	35,2	81,2	8,8	—	—	9,6

*The reaction conditions are the same as those in Table 1.

The formation of aldehydes can be explained by the hydrogenation of MA, and of acetic acid by the carbonylation of methanol formed together with acetaldehyde on hydrogenation of MA:

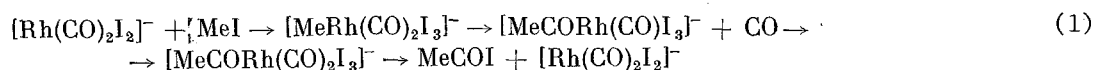


By increasing the CO pressure from 50 to 100 atm the yield of AA rises from 63 to 97.8%, and then decreases to 84.5% for a CO pressure equal to 120 atm. By changing the reaction temperature from 100 to 230°C the yield of AA passes through a maximum (97%) at 200°C, and then decreases to 90% at 230°C (Fig. 1).

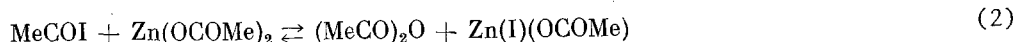
The optimum MeI content in the initial reaction mixture is in the region 35-50% (see Fig. 1).

In the IR spectra of the reaction mixtures after conducting the carbonylation reactor of MA under optimum conditions (200°C, 100 atm), clearly defined absorption bands in the region 2000-2100 cm⁻¹ were observed, corresponding to frequency vibrations of carbonyl groups in carbonylhalide complexes of metals [6-8], as well as bands characteristic of AA: 1820, 1760, 1431, 1370, and 1295 cm⁻¹ [6-8].

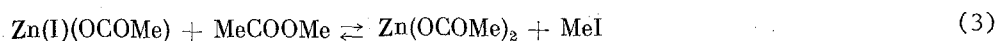
On the basis of the data of [9], and also the results obtained by us, we assumed that under the reaction conditions metal carbonylhalide complexes are formed from RhCl₃·3H₂O, CO, and iodide-containing promotor; in particular, the [Rh(CO)₂I₂]⁻ complex is responsible for catalysis. The reaction mechanism of carbonylation includes a number of stages:



MeCOI formed according to Eq. (1) is then converted to AA by reaction with Zn acetate:



In the final stage of the catalytic cycle Zn acetate and MeI are regenerated by interaction of Zn iodide monoacetate, formed as an intermediate, with initial MA:



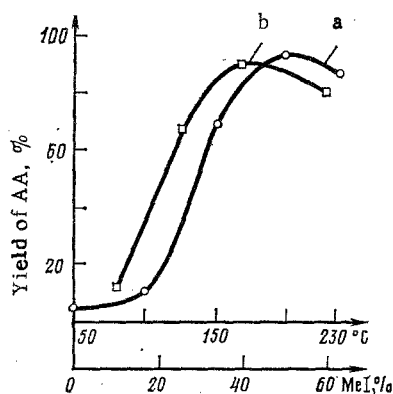
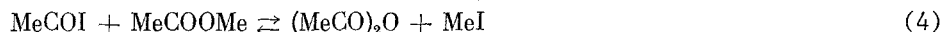


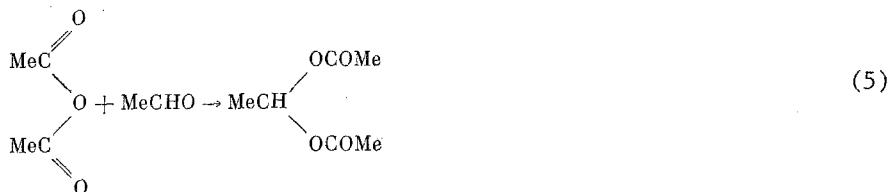
Fig. 1. Dependence of yield of AA by carbonylation of MA on: a) temperature; b) MeI content in the initial reaction mixture.

The reversibility of stage (3) was confirmed by a special experiment in which by interaction of 18.3 g (0.1 mole) Zn acetate with 28.4 g (0.2 mole) MeI in an atmosphere of N_2 ($170^\circ C$, $p_{N_2} = 60$ atm, $\tau = 2$ h) quantitative formation of Zn iodide monoacetate and MA was observed. ZnI_2 is not formed, despite the presence of a sufficient quantity of MeI for its formation. The presence of $Zn(I)(OCOMe)$, MA, and MeI in the reaction mixture was established by GLC analysis. Found: C 10.51; H 1.39; I 51.12%. $C_2H_3O_2IZn$. Calculated: C 9.50; H 1.20; I 50.50%.

In the absence of Zn acetate, AA is formed from MA according to the equation



For verification of the present mechanism for formation of AA from MA and CO in the presence of the catalytic system $RhCl_3-Zn(OCOCH_3)_2-MeI$, experiments were conducted with deuterated Zn acetate, which was prepared from ZnO and CD_3COOD . In the mass spectrum of AA obtained using $Zn(OCOCD_3)_2$ were observed masses characteristic of $(MeCO)(CD_3CO)O$, as well as of partially deuterated EDA formed in small quantities (1-3%) as a result of the reaction



Acetaldehyde is formed by hydrogenation of MA with hydrogen generated by the water gas reaction.

In the mass spectrum of AA obtained by using CD_3I (prepared from CD_3OD , I_2 , and dry red phosphorus [10]) are found masses characteristic of AA, m/z 46 (CD_3CO) and m/z 43 ($MeCO$); this indicates the formation of partially deuterated AA with composition $(MeCO)(CD_3CO)O$. An intense molecular ion M^+ (149) corresponding to deuterated EDA $MeCH(OCOMe)(OCOCD_3)$, and

mass m/z relating to the $MeCH$ fragment, were observed. In the IR spectrum of

AA obtained using $Zn(OCOCD_3)_2$ or CD_3I , a displacement of CH_3 group absorption bands is observed, which indicates the presence of the CH_3 group in the molecule of AA formed. Elemental analysis of AA obtained by carbonylation of 0.13 mole MA (yield of AA 90%) in the presence of 0.1 g $RhCl_3 \cdot 3H_2O$, 0.016 mole $Zn(OCOMe)_2$, and 0.079 mole CD_3I also confirmed the proposed reaction mechanism. Analysis showed a 25% enrichment of AA with deuterium. Found: C 46.8; H 7.21%. $C_2H_2D_3O_6$. [1:1 mixture of $(MeCO)_2O + (CD_3CO)(MeCO)O$]. Calculated: C 46.4; H 7.23%. Taking into account the fact that the molar ratio of Zn acetate to MeI during the course of reaction must remain constant, the theoretical percentage of deuterium enrichment of AA for 100% yield must amount to about 30% $[(0.079/2:0.13) \cdot 100 = 30\%]$.

CONCLUSIONS

1. It was found that the activity and selectivity of halides of rhodium, ruthenium, and palladium for carbonylation of methyl acetate to acetic anhydride vary according to the series: $\text{RhCl}_3 > \text{RuCl}_3 > \text{PdCl}_2$.
2. The optimum conditions for synthesis of acetic anhydride by carbonylation of methyl acetate have been found.
3. A reaction mechanism has been proposed for the carbonylation of methyl acetate with formation of acetic anhydride in the presence of a catalytic system consisting of rhodium(III) chloride, zinc acetate, and methyl iodide.

LITERATURE CITED

1. Organic Reactions [Russian translation], Vol. 5, Moscow (1956), p. 126.
2. US Patent No. 4002677 (1977); US Patent No. 4002678 (1977).
3. German Patent Application No. 2450965 (1976).
4. Japanese Patent No. 52-3926 (1976); Japanese Patent No. 16-91205 (1976); Chem. Abs., 85, 142680 (1976).
5. German Patent No. 2856791 (1979); Chem. Abs., 91, 108459 (1979).
6. A. N. Nesmeyanov (ed.), Organic Syntheses via Metal Carbonyls [Russian translation], Mir, Moscow (1970).
7. R. Mecke and F. Langerbucher, Infrared Spectra of Selected Chemical Compounds, Vol. 1, London (1965).
8. J. C. Lavalley, J. Sanssey, and T. Rais, J. Mol. Catal., 17, No. 2-3, 289 (1982).
9. A. I. Vogel, A Text Book of Practical Organic Chemistry Including Qualitative Organic Analysis, London-New York (1956), p. 287.
10. Z. Hauptman, J. Greife, and H. Remane, Organic Chemistry [Russian translation], Khimiya, Moscow (1979), pp. 298-299.

SYNTHESIS OF HIGHER EPOXIDES BY THE JOINT CATALYTIC OXIDATION OF ALDEHYDES AND OLEFINS

M. G. Vinogradov, I. P. Kovalev, and G. I. Nikishin UDC 542.943.7:547.28+547.313

The epoxidation of olefins was previously accomplished by the joint oxidation of acetaldehyde with propylene in benzene and CCl_4 with oxygen at a pressure of 50 atm at 70-80°C in the absence of a catalyst [1, 2], by the joint oxidation of AcH with the C_3 - C_{18} olefins in the presence of salts of Fe [3] or Co [4], and from isobutyraldehyde with propylene in the presence of salts of Ti or Co [5] at an oxygen pressure of 3-15 atm at 70-140°C. The utilization of a significant excess of the olefin relative to the aldehyde in these reactions lead to the partial polymerization of the olefin, and the selectivity of formation of the corresponding epoxide comprises 5-15%.

We developed a method for the joint catalytic oxidation of C_2 - C_5 aliphatic aldehydes and the C_7 - C_{10} 1-alkenes permitting the selective isolation of 1,2-epoxides or the monoesters of 1,2-diols [6].

In order to suppress the secondary polymerization of the olefins, we carried out the reaction with a 2-10 times excess of the aldehyde relative to the olefin. Salts of Fe(III), Co(II), Mn(II), Ni(II), Cu(II), and Zr(IV) (Table 1) were utilized as catalysts of the epoxidation. The solvents utilized were AcOH and PrCOOH .

The reaction of the joint catalytic oxidation of butyraldehyde with 1-heptane was studied in the greater detail. The main product of this reaction is 1,2-epoxyheptane (I) which,

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 10, pp. 2269-2272, October, 1985. Original article submitted August 2, 1984.