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OXAMIDE FORMATION BY THE REACTION OF SILVER ACETATE, AMINE AND CARBON MONOXIDE

Takeo Saegusa, Tetsuo Tsuda, Katsuhiko Isayama, Kiyoaki Nishijima and Yo Isegawa
Department of Synthetic Chemistry, Faculty of Engineering,
Kyoto University, Kyoto, Japan

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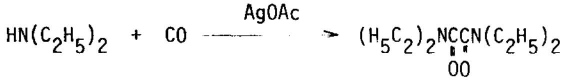
Recently we studied the reaction of quarternary system consisting of metallic acetate, amine, carbon monoxide and methanol. The reaction systems containing mercuric, thallic and cupric acetates as the metallic acetate component gave urethane in preference to formamide. On the contrary, silver acetate produced formamide as a main product and urethane in trace amounts.[1)] In these reactions, amine and methanol were used in large excess to metallic acetates. In the present communication we report the formation of oxamide in the three components reaction of silver acetate, diethylamine and carbon monoxide in the absence of methanol.



$$HN(C_2H_5)_2 + CO \xrightarrow{AgOAc} (H_5C_2)_2N\underset{O}{\overset{}{C}}\underset{O}{\overset{}{C}}N(C_2H_5)_2$$

To a high pressure vessel, silver acetate, diethylamine and reaction solvent were added at room temperature, to which carbon monoxide was compressed up to 75 kg./cm.^{2} at -78°C. The tube was closed and heated at the desired temperature. Then carbon monoxide was purged off. The reaction mixture was immediately distilled without filtration. The first fraction of distillation boiling at temperatures up to 140°C under atmospheric pressure contained reaction solvent and unreacted diethylamine, and the second fraction at temperatures up to 180°C under 1 mmHg consisted of the carbonylated products. The second fraction was analyzed by gas chromatography. Oxamide (N,N,N',N'-tetraethyloxamide), formamide (N,N-diethyl formamide), urea (N,N,N',N'-tetraethylurea) and acetamide (N,N-diethyl acetamide) were obtained as the reaction products. Oxamide was isolated by preparative gas chromatography and identified by nmr and ir spectra analyses and also by the comparison of the retention time of gas chromatography with the authentic sample. Formamide, urea and acetamide were identified by the comparisons of the retention times of gas chromatography with the corresponding authentic samples. The experimental results are summarized in Table I.

Table I. Reaction of silver acetate, diethylamine and carbon monoxide

AgOAc	$HN(C_2H_5)_2$	Solvent	Time	Temp.	Yields of Products (%)a)			Recovered
(mole)	(mole)	(ml.)	(hr.)	(°C)	oxamide	formamide	acetamide	$HN(C_2H_5)_2$ (%)
0.01c)d)	0.01	triethylamine , 7	19	160	2	4	13	not determined
0.02c)d)	0.02	〃 ,14	21	115	1	7	19	〃
0.01c)d)	0.01	〃 , 7	24	110	1	5	20	〃
0.01c)d)	0.01	〃 , 7	24	room temp.	10	2	18	〃
0.02c)d)	0.02	〃 , 7	21	0	10	1	1	〃
0.02c)d)	0.01	〃 ,14	25	room temp.	16	4	2	〃
0.02c)d)	0.02	〃 ,14	25	〃	10	4	3	〃
0.02c)d)	0.04	〃 ,14	25	〃	10b)	8b)	2b)	〃
0.02d)	0.02	〃 ,14	22	〃	11	4	4	24
0.02e)	0.02	〃 ,14	26	〃	24	5	2	not determined
0.06f)	0.03	〃 ,42	21	〃	38	3	11	〃
0.06f)	0.03	〃 ,42	63	〃	40	6	10	〃
0.02e)	0.02	tetrahydrofuran ,16	44	〃	31	5	4	〃
0.06f)	0.03	〃 ,42	18	〃	34	3	7	〃
0.04f)	0.02	ethyleneglycol dimethylether ,20	21	〃	40	1	1	〃
0.02e)	0.02	pyridine ,16	23	〃	3	3	trace	〃
0.02e)	0.02	N,N,N',N'-tetramethyl ethylenediamine ,15	23	〃	4	2	〃	71

a) The yields of products are based on diethylamine.
b) The yield of product is based on silver acetate.
c) The reaction mixture was filtrated before the distillation.
d) The reaction was carried out in a 50 ml. stainless steel tube without shaking or stirring under carbon monoxide pressure of 60~75 kg./cm.^{2}.
e) The reaction was carried out in a mechanically-shaked 50 ml. stainless steel tube under carbon monoxide pressure of 60~70 kg./cm.^{2}.
f) The reaction was carried out in a magnetically-stirred 100 ml. stainless steel autoclave under carbon monoxide pressure of 60~70 kg./cm.^{2}.

Among the products urea was formed only in trace amounts. Oxamide was formed as a main product in low temperature reactions. High reaction temperature is unfavorable for the oxamide formation. Several silver salts were examined in their reactivities toward the present reaction (Table II). It is shown that only silver acetate is effective for the carbonylation.

Table II. Reaction of silver salts, diethylamine and carbon monoxide[a)]

Silver salt (mole)	$HN(C_2H_5)_2$ (mole)	Solvent (ml.)	Time (hr.)	Temp. (°C)	Yields of Products (%)[b)]		
					oxamide	formamide	acetamide
AgOAc[c)] , 0.02	0.02	triethylamine, 14	26	room temp.	24	5	2
AgCl , 0.02	0.02	〃 , 14	17	〃	1	trace	trace
AgSCN , 0.02	0.02	〃 , 14	20	〃	trace	〃	〃
AgCN , 0.02	0.02	〃 , 14	23	〃	〃	〃	〃

a) The reactions were carried out in a mechanically-shaked 50 ml. stainless steel tube under carbon monoxide pressure of 65 kg./cm.^{2}.
b) The yields of products are based on diethylamine.
c) See Table I.

The oxamide formation was observed by Tsuji[2)] in the reaction of amine and carbon monoxide with palladium compound catalyst at 180°C. The silver acetate-amine-carbon monoxide reaction of the present study is characterized by the formation of oxamide at much lower temperatures.

As to the mechanism of the oxamide formation, it may be assumed that the reaction intermediate, $Ag\underset{\overset{\|}{O}}{C}N(C_2H_5)_2$, is formed and the coupling of two $-\underset{\overset{\|}{O}}{C}N(C_2H_5)_2$ groups produces oxamide.

In the case of mercuric salts, the compounds having $Hg\text{-}\underset{\underset{O}{\|}}{C}NR_2$ bond have been isolated by the reactions of mercuric salts with amine and carbon monoxide.3),4) Mechanistic study and extention of this work are being made now.

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