BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1499—1502 (1967)

Thallic Salt as the Catalyst for the Conversion of Acetylenes to Carbonyl Compounds

Sakae UEMURA, Ryohzoh KITOH, Koichi FUJITA and Katsuhiko ICHIKAWA

Institute for Chemical Research, Kyoto University, Sakyo-ku, Kyoto

(Received December 5, 1966)

It has been shown that the conversion of acetylenes to carbonyl compounds proceeds in various solvents containing thallic salts as the catalyst. Acetylene, methylacetylene, phenylacetylene, propargyl alcohol and its ester, and phenylpropiolic acid and its ester reacted to form acetaldehyde, acetone, acetophenone, acetoxyacetone and acetophenone respectively.

In the reaction of olefins, it has been observed that thallic and mercuric salts show similar chemical behavior.[1] It is desirable to study, therefore, whether the same tendency can be expected or not in the reactions of acetylenes with both these metal salts. This paper describes the experimental results that thallic salts can be the catalyst for the conversion of acetylenes to carbonyl compounds as mercuric salts.

For the experimental convenience, detailed experiments have been carried out with phenylacetylene. Since a literature shows that phenylacetylene is the most reactive for the above reaction and forms acetophenone by treating with aqueous sulfuric acid at room temperature[2] or by heating with water at 325°C,[3] the experiments with mineral acid catalyst have been made as the control experiments to evaluate the activities of thallic salts. The results obtained are summarized in Table 1.

At the same catalyst concentration and reaction temperature, thallic salts are much more active than the mineral acids. Among thallic salts, the chloride is the most effective and the best result was obtained in glacial acetic acid. As the water contents of acetic acid increased, the yields of acetophenone decreased, and the reaction did not proceed in water. Probably this is partly due to the decrease of solubility of phenylacetylene in the solvent. Catalytic activities in 97% acetic acid decreased in the order of chloride, sulfate and acetate. With nitrate, only very low yields of acetophenone were obtained and the product contained larger amounts of high boiling materials, and thallic was reduced to thallous ion completely after the reaction. It seems likely that the oxidation of phenylacetylene is the predominant reaction in this case.

In ethanol solvent and with thallic chloride, the yield of acetophenone was low and a considerable amount of resinous product was formed, despite of the fact that no remarkable extent of oxidation was observed since thallic ion concentration remained almost unchanged after the reaction. This appears to be important for the mechanistic consideration of the reaction intermediate, because only small amounts of high boiling product were formed in the cases of acetic acid solvent.

It is interesting to compare these results with those of mercuric salt catalysis, and the data obtained under the corresponding conditions are listed in Table 1. In sharp contrast with the cases of thallic chloride and acetate, mercuric chloride and acetate showed no activity in glacial acetic acid. The best yield of acetophenone was obtained with mercuric sulfate. With mercuric nitrate, oxidation proceeded predominantly as in the case of thallic nitrate.

According to the literature,[4] phenylacetylene forms α-acetoxystyrene as the major product and acetophenone as the minor one in acetic acid containing catalytic amounts of mercuric acetate and boron trifluoride. The result of our experiment, using thallic acetate in place of mercuric acetate under the same conditions, showed that no reaction took place and only phenylacetylene was recovered. In connection with this, it must be added that thallic acetate or chloride was found to catalyze the conversion of α-acetoxystyrene to acetophenone (see Experimental Part).

Residual concentrations of trivalent thallium after the reaction were determined by iodometry,[5] because its decrease means the loss of the activity

---

[1] See, for example, K. Ichikawa, S. Uemura and T. Sugita, *Tetrahedron*, **22**, 407 (1966); S. Uemura, R. Kitoh and K. Ichikawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **87**, 986 (1966).

[2] C. Friedel and M. Balsohn, *Bull. soc. chim. France*, [2], **35**, 55 (1881).

[3] A. Desgrez, *Ann. Chim.*, [7], **3**, 231 (1894).

[4] A. I. Bol'shukin and V. L. Zhitorchuk, *Zhur. Obshchei Khim.*, **25**, 1459 (1955); *Chem. Abstr.*, **50**, 4832 (1956).

[5] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd Ed., MacMillan, N. Y. (1961), p. 585.

TABLE 1. CONVERSION OF PHENYLACETYLENE TO ACETOPHENONE
(Phenylacetylene, 10 g)

Catalyst g	Solvent (80 m*l*)	Temp. °C	Time hr	$C_6H_5COCH_3$ yield %	$C_6H_5C{\equiv}CH$ recovered %	Residual Tl^{3+} %
HCl (1 M)	H_2O	60	3	0	85	
(0.07 M)	HOAc, 100%	60	3	3	61	
(1 M)	HOAc, 100%	60	3	81	0	
H_2SO_4 (1 M)	HOAc, 100%	60	3	60	0	
$TlCl_3 \cdot 4H_2O$						
2 (0.07 M)	HOAc, 100%	60	3	35	48	69
2	HOAc, 97%	60	3	32	40	52
2	HOAc, 90%	60	3	22	60	24
2	HOAc, 50%	60	3	15	57	47
2	H_2O	60	3	0	70	90
2	HOAc, 97%	60	11	82	0	32
2	HOAc, 90%	100	3	84	3	73
2	HOAc, 100%	100	1	76	10	98
1	HOAc, 90%	100	1	68	20	
0.5	HOAc, 90%	100	1	39	43	
0.1	HOAc, 90%	100	1	5	80	
0	HOAc, 100%	60	10	0	85	
2	C_2H_5OH	60	10	20	0	90
$Tl_2(SO_4)_3 \cdot 7H_2O$						
2 (0.027 M)	HOAc, 97%	100	1	66	16	37
2	HOAc, 97%	60	3	20	53	59
2	HOAc, 97%	15	8	trace	54	23
$Tl(NO_3)_3 \cdot 3H_2O$						
2 (0.05 M)	HOAc, 97%	60	3	2	41	0
2	HOAc, 97%	15	5.5	0	45	0
$Tl(OAc)_3$						
2 (0.058 M)	HOAc, 100%	60	13.5	23	61	30
2	HOAc, 100%	60	3	1	71	26
2	HOAc, 97%	60	3	4	88	28
5	HOAc, 100%	65	11	67	0	11
30	HOAc, 100%	60—80	13[a]	82	13	30
$Hg(OAc)_2$						
2	HOAc, 100%	60	11	trace		
$HgCl_2$						
2	HOAc, 100%	60	3	0		
$HgSO_4$						
2	HOAc, 97%	60	3	79		
$Hg(NO_3)_2 \cdot 1/2H_2O$						
2	HOAc, 97%	60	3	3.4		

a) At 60°C for 6 hr and then at 80°C for 7 hr.

due to oxidation. However, no definite tendency to relate the data to the reaction temperature nor the yields of acetophenone has been observed, as far as the present results are concerned.

As the other examples, phenylpropiolic acid, propargyl alcohol and their ester, methylacetylene and acetylene were used as the substrates.

In glacial acetic acid containing thallic chloride, phenylpropiolic acid gave acetophenone in 52% yield by a reaction at 80°C for 10 hr. With thallic acetate the yield was much higher (92%). Acetophenone appears to have resulted from decarboxylation of benzoylacetic acid which was formed primarily, and not from phenylacetylene which might be formed by decarboxylation of the substrate, since no acetophenone nor phenylacetylene were formed from phenylpropiolic acid under the same conditions without thallic salt. At the same temperature, methyl ester of the acid formed only a trace of acetophenone by the reaction with thallic acetate for 7 hr. Thallic chloride was much more active and the yields of acetophenone were 26 and 71% at 80°C (7 hr) and 100°C (10 hr) respectively.

Propargyl acetate gave acetoxyacetone in 45% yield by a reaction in glacial acetic acid containing thallic chloride at 100°C for 3 hr. With thallic acetate the yield was lower (32%). With thallic chloride and at 100°C, propargyl alcohol reacted to form acetoxyacetone and propargyl acetate in the same solvent. The yields of the former were not improved by increasing the reaction time from 1 to 5 hr, because trivalent thallium was reduced completely to monovalent already after 1 hr's reaction. The yield was only 5%. On the other hand, thallium salt appears to accerelate the esterification of the alcohol, since the yields of the latter were 37 and 58% (on the basis of the alcohol charged) after the reaction times of 1 and 5 hr, while, in the absence of thallium salt, only 5% yield of the ester was obtained under the same conditions in 1 hr. With thallic acetate, the yields of acetoxyacetone were improved slightly and were 11 and 13% after the reaction times of 1 and 5 hr. The yields of propargyl acetate in these cases were 16 and 17% respectively. Thallic ion could not be detected after the reaction time of 1 hr in this case as in the case of chloride. The best yield of acetoxyacetone (22%) was obtained by a reaction in a boiling acetic acid containing thallic acetate in a short reaction time (0.1 hr). It seems likely that oxidation of alcohol proceeds more rapidly than the carbonyl formation.

Methylacetylene at a rate of 2 *l*/hr were bubbled into glacial acetic acid containing thallic salts at various temperatures for 4 hr. With chloride, the yields of acetone were 1.7, 2.6 and 4.4 g and the amounts of residual thallic ion unchanged after the reaction were 90, 50 and 10% at 30, 60 and 100°C respectively. With acetate (60°C, 6 hr) and sulfate (60°C, 2 hr), the yields of acetone were 18 and 4% respectively. No quantitative experiment to determine the yield was carried out.

Acetylene reacted to form acetaldehyde by bubbling into aqueous sulfuric and glacial acetic acids containing thallic salts, and approximate yields were calculated on the basis of rough material balance. The best yield (15%) was obtained with thallic sulfate dissolved in 45% sulfuric acid at 70°C. In order to compare the activity with that of mercuric sulfate, the reaction carried out under the same conditions. Since the yield with mercuric salt was 40%, it seems likely that mercuric salt is more effective than thallic salt as far as the case of acetylene is concerned. In 97% acetic acid, only thallic chloride showed catalytic activity, although the yield of acetaldehyde was only 13% at 100°C.

As the conclusion from the above results it can be mentioned that, with terminal acetylenes, carbonyl group is formed at inner carbon, even in the cases of the substituents such as hydroxymethyl and acetoxymethyl which are considered to be more electronegative than methyl and phenyl groups. This direction is the same as that of the case with mercuric salt catalyst.6)

Experimental

Materials. Acetic acid, ethanol, phenylacetylene, propargyl alcohol and its acetate were commercial products and used after distillation. Acetylene and methylacetylene were also commercial ones and used without further purification. Phenylpropiolic acid was prepared by dehydrobromination of ethyl α, β-dibromo-β-phenylpropionate with alkali as described in the literature, mp 135.5—137.5°C (from chloroform).7) Methyl ester of the acid was obtained by the reaction of diazomethane with the acid in ether, bp 90—94°C/2 mmHg, n_D^{20} 1.5630 (reported, n_D^{25} 1.5618).8) Thallic acetate (anhydrous) was prepared by the method proposed by Grinstead,9) and dried over phosphorus pentoxide. Thallic chloride ($TlCl_3 \cdot 4H_2O$) and oxide were commercial products. Thallic nitrate ($Tl(NO_3)_3 \cdot 3H_2O$) and sulfate ($Tl_2(SO_4)_3 \cdot 7H_2O$) were prepared by dissolving the oxide into the corresponding hot acids and collecting white crystals after cooling.

Conversion of Acetylenes to Carbonyl Compounds. All experiments were carried out in 80 m*l* of solvents containing 2 g of salts, unless otherwise described. With liquid and solid substrates, 10 g of samples were used. Experimental procedure is shown by the following typical example.

Acetophenone from Phenylacetylene. Into a clear solution of 80 m*l* of aqueous acetic acid (10% water) containing 2 g of thallic chloride at 100°C, 10 g of phenylacetylene was added slowly. Evolution of reaction heat was observed and cooling was required to maintain the reaction temperature. Color of the reaction mixture became green at first and then turned to brown with simultaneous formation of a small amount of white precipitate. After 3 hr at this temperature, the reaction mixture was cooled to room temperature and filtered to remove the precipitate (0.93 g). The filtrate was diluted with water and extracted with ether. The extract was washed with saturated sodium bicarbonate solution, dried over sodium sulfate and distilled. Together with 0.3 g of recovered phenylacetylene, 9.92 g of acetophenone (84% yield of the theoretical amount) was obtained, bp 100—107°C/34 mmHg, mp of 2, 4-dinitrophenylhydrazone, 248—250°C (reported, 250°C).10) IR and UV spectra and the retention time of gas chromatographical analysis were identical with those of the authentic sample.

Acetoxyacetone. Reaction mixtures with propargyl alcohol and its acetate were diluted, filtered and

---

6) G. F. Hennion and W. S. Murray, *J. Am. Chem. Soc.*, **64**, 1220 (1942); R. N. Haszeldine and K. Leedham, *J. Chem. Soc.*, **1952**, 3483.

7) T. W. Abbott, "Organic Syntheses," Coll. Vol. II, p. 515.

8) I. Heilbron, "Dictionary of Organic Compounds," Vol. IV, Oxford Univ. Press, N. Y. (1953), p. 159.

9) R. R. Grinstead, *J. Org. Chem.*, **26**, 238 (1961).

10) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "Systematic Identification of Organic Compounds," 4th Ed., Wiley, N. Y. (1956), p. 317.

extracted with ether by a continuous extracting apparatus. Distillation of the extracts gave acetoxyacetone, bp 66—72°C/10 mmHg, n_D^{20} 1.4164 (reported, 1.4150).[11] (Found: C, 51.90; H, 7.22%. Calcd for $C_5H_8O_3$: C, 51.72; H, 6.94%). NMR: τ 5.32 and 7.81 (relative intensities, 2 : 6) in deuteriochloroform.

Acetone. Reaction mixtures with methylacetylene were treated as described above. Distillation of the extracts gave acetone, bp 54.5—56.5°C, mp of 2, 4-dinitrophenylhydrazone, 125.3—126°C (reported, 126 °C).[12] No other product could be detected except resinous residue in the reactions at higher temperatures.

Acetaldehyde. In the case of sulfuric acid solution, the reaction mixtures of acetylene were oxidized to convert acetaldehyde to acetic acid and distilled. From the results of alkali titration of the distillates, yields of acetaldehyde were calculated according to the method proposed by Neumann and Schneider.[13] In the case of 97% acetic acid solvent, the reaction mixtures were distilled after diluting with water. Acetaldehyde contents of the distillates were determined gravimetrically by 2, 4-dinitrophenylhydrazone method, mp 165—168°C (reported, 168°C).[14]

Conversion of α-Acetoxystyrene to Acetophenone. Into 80 m*l* of glacial acetic acid containing 2 g of thallic chloride 5.7 g of α-acetoxystyrene (prepared by the method reported by Bol'shukin *et al.*,[5] bp 86—89°C/4 mmHg, n_D^{20} 1.5333) was dissolved and kept at 60°C for half an hour, and worked up as in the case of phenylacetylene. Acetophenone was obtained in 78% yield. Unreacted α-acetoxystyrene could not be detected by gas chromatographical analysis. The result of trivalent thallium analysis after the reaction showed that no reduction of thallic ion occurred. With thallic acetate, 90% yield of acetophenone was obtained by the same reaction at 60°C for 4 hr.

---

[11] Ref. 8, Vol. I, p. 19.

[12] Ref. 10, p. 316.

[13] B. Neumann and H. Schneider, *Angew. Chem.*, **33**, 189 (1920).

[14] Ref. 10, p. 283.