The Preparation and Stoichiometric Synthetic Reactions of Metal Methanesulfonate Salts

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This paper presents a comprehensive review of the preparation and use as stoichiometric reagents of metal methanesulfonate salts. A number of commercial operations produce various metal methanesulfonate salts on a large scale, and new preparative processes and product offerings are being developed all the time. Most of the work in this field focuses on the use of metal methanesulfonate compounds as components of electroplating solutions and as catalysts. However, there are also a limited number of significant applications of metal methanesulfonate salts as stoichiometric reagents for organic synthesis. It behooves the preparative chemist to stay current with all the potential applications of easily obtained commercially available materials, and it is the intention of this article to give a comprehensive review of the possible uses of metal methanesulfonates as stoichiometric reagents.

Keywords: Metal methanesulfonate, metal mesylate, methanesulfonic acid, stoichiometric reagent, salt preparation, salt synthesis, stoichiometric reagent

Introduction:

Metal methanesulfonate salts are employed in a number of diverse procedures. This paper aims to comprehensively review two areas: the methods by which metal methanesulfonates and their simple solvates can be prepared, and the preparative procedures in which a stoichiometric amount of a metal methanesulfonate salt is used. The reactions to be covered include those wherein a mesyloxy group is added and also those wherein the unique physical properties of the methanesulfonate anion are critical for the success of a reaction that employs a stoichiometric amount of a metal salt. This paper will not cover the use of metal methanesulfonates as part of the electrolyte in electroplating and metal finishing applications. Also, this paper will not, with a few exceptions, cover the use of metal methanesulfonates as catalysts and as components of formulated mixtures. The coverage of pharmaceutical onium compounds will be limited to those cases wherein the preparation involves a discrete metal methanesulfonate salt.

The Preparation of Metal Methanesulfonates:

The general procedures that have been adapted for the preparation of metal methanesulfonate salts are described below. A total of nine generic methods (A - I) have been identified. These generic methods are referenced in the comprehensive listing of preparative methods cataloged in Table 3 of this paper. Note that the abbreviation MSA is used to denote methanesulfonic acid, and OMs, OMs⁻ in ionized form, is used to denote the methanesulfonate anion.

A) The reaction of MSA with a basic metal (oxide, hydroxide or carbonate) salt:

This is oftentimes the simplest laboratory scale method for the preparation of metal methanesulfonate salts. The general method is illustrated by the following reactions.
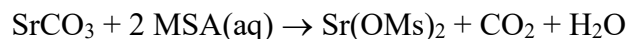
Silver methanesulfonate from silver oxide,[1]

$$Ag_2O(s) + 2\ MSA(aq) \rightarrow 2\ AgOMs(aq) + H_2O$$
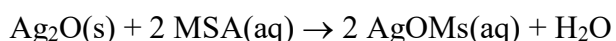
Lithium methanesulfonate from lithium hydroxide,[1]

$$LiOH(aq) + MSA(aq) \rightarrow LiOMs(aq) + H_2O$$
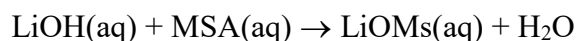
Strontium methanesulfonate from strontium carbonate,[1]

$$SrCO_3 + 2\ MSA(aq) \rightarrow Sr(OMs)_2 + CO_2 + H_2O$$

The driving force for these reactions is the release of chemical potential that accompanies the conversion of strongly acidic and basic reactants to less strongly acidic and basic products. In general, a slight excess of either the MSA or the basic metal salt is employed. When an excess of MSA is used, one must take steps to insure that the excess acid is removed from the final product. This acid removal can be accomplished by recrystallizing the final product from an appropriate solvent, usually water, or by washing the final product with a hydrophilic organic solvent (*e.g.*, ethanol, acetone). When an excess of a soluble basic metal salt is employed, one must recrystallize the final product from water. In general, the use on excess of a soluble basic metal salt is not recommended, as a purer product and higher yield are possible via the use of a slight excess of MSA. When an excess of an insoluble basic metal salt is employed, one must, following completion of the reaction, filter the excess basic salt from the product. The use of an excess of the basic metal salt allows for the preparation of very pure monovalent metal methanesulfonates (*e.g.*, AgOMs), but in the case of polyvalent metals there is the possibility that some mixed oxide/methanesulfonate type product will be formed. In many cases, the reaction of even an excess of MSA is slow to react with certain basic metal salts, and in these cases one must both filter the final reaction solution to remove residual basic metal salt and take measures to remove excess MSA. For basic metal salts containing a hydrolytically unstable metal cation, anhydrous MSA or neat methanesulfonic anhydride are sometimes used in place of MSA(aq). As a final purification step, the solid product is oftentimes heated under vacuum to remove residual solvent, excess water and/or water of hydration. The following procedures are illustrative:[1]

Lithium Methanesulfonate, (LiOMs): Lithium hydroxide monohydrate (42 g, 1 mole) was slowly added to 70% aqueous MSA (140 g, 1 mole) over 10 minutes with stirring. The homogeneous solution was evaporated *in-vacuo* (4 mm Hg) to a solid residue, and the solid residue was washed with acetone and ether. The remaining solid product was reduced to a constant weight by heating to 100 °C at 1 mm Hg vacuum (81% yield of LiOMs). LiOMs, %Li/%S (theoretical) = 0.22, %Li/%S (actual) = 0.21, analysis by ICP/emission for %Li and %S.

Calcium Methanesulfonate, Ca(OMs)$_2$: To a 1 liter beaker charged with 70% aqueous MSA (310 g, 2.26 moles, 3% excess) heated to 90 °C was added finely powdered CaCO$_3$ (110 g, 1.10 moles) with stirring over about one hour. When the addition was complete, the temperature was brought to 100 °C and DI H$_2$O was added until the solution became clear. The clear solution was decanted away from any remaining solid material and evaporated *in-vacuo* (4 mm Hg) to a solid residue. The solid residue was washed with solvent (isopropyl alcohol and ether) and evaporated to constant weight *in-vacuo* (1 mm Hg). The yield of Ca(OMs)$_2$ was 37%. Ca(OMs)$_2$, %Ca/%S (theoretical) = 0.63, %Ca/%S (actual) = 0.62, analysis by ICP/emission for %Ca and %S.

Strontium Methanesulfonate, Sr(OMs)$_2$: A 500 ml beaker was charged with 70% aqueous MSA (75 g, 0.547 moles, 40% excess), powdered strontium carbonate (25 g, 0.160 moles), and DI H$_2$O (20 ml). The mixture was stirred at RT overnight and then filtered through a 1 micron glass microfiber pad. The clear filtrate was evaporated *in-vacuo* (4 mm Hg) to a crystalline residue. The crystalline residue was washed with isopropyl alcohol and ether. The solid product was evaporated to constant weight *in-vacuo* (1 mm Hg). The yield of Sr(OMs)$_2$ was 95%.

Silver Methanesulfonate, (AgOMs): To 500 g of 70% aqueous MSA (3.64 moles) in a 1 gallon beaker, 402 g of silver oxide (3.47 moles of Ag^+) was slowly added over 30 minutes to form a uniform suspension. The temperature mixture rose to approximately 60 °C during the addition, and this temperature was maintained with heating for an additional 4 h. The reaction mixture was filtered a 1 micron glass microfiber pad to remove residual silver oxide (solution refiltered if necessary), and the filtrate was stripped *in-vacuo* (4 mm Hg) to a solid residue. The solid residue was washed with isopropyl alcohol and ether. The final product was reduced to constant weight *in-vacuo* (1 mm Hg). The yield of AgOMs was approximately 64%. AgOMs, %Ag/% S (theoretical) = 3.36, %Ag/%S (actual) = 3.37, analysis by ICP/emission for %Ag and %S.

It is possible to use metal salts that are significantly more basic than simple metal oxides, hydoxides and/or carbonates for the preparation of metal methanesulfonates. For instance, sodium ethoxide has been employed for the preparation of sodium methanesulfonate.[2] However, such strongly basic compounds (*e.g.,* BuLi, potassium *tert*-butoxide) are usually air and moisture sensitive, and any benefits gained from increased reactivity are offset by the disadvantages associated with handling expensive, flammable and potentially explosive materials. The use of basic metal sulfides, while possible, is not recommended, as the handling of the co-product H_2S is problematic. In the processing of mined ores, it has been found that the extraction of galena (PbS) containing crude ore concentrates with MSA yields, among other things, lead methanesulfonate,[3]
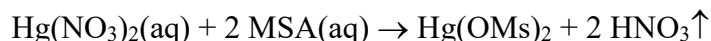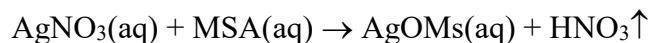
$$PbS + 2\ MSA \rightarrow Pb(OMs)_2 + H_2S$$
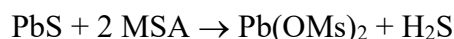
The process requires that the PbS containing crude ore concentrate be steeped in hot concentrated MSA(aq) for several days. The purity of the lead methanesulfonate produced depends upon the purity of the ore concentrate employed, but typically it is not considered pure.

B) The reaction of methanesulfonic acid with a neutral or acidic metal salt:
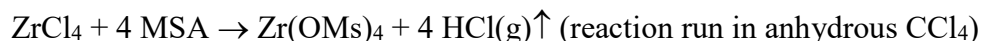
This method can be used conveniently for the preparation of hydrolytically unstable metal methanesulfonates (*e.g.,* Ti^{+4}, Zr^{+4}), and this method is sometimes the easiest way to produce anhydrous materials.

The general method is illustrated by the following reactions.

Silver and mercuric methanesulfonate from silver and mercuric nitrate,[1]

$$AgNO_3(aq) + MSA(aq) \rightarrow AgOMs(aq) + HNO_3\uparrow$$

$$Hg(NO_3)_2(aq) + 2\ MSA(aq) \rightarrow Hg(OMs)_2 + 2\ HNO_3\uparrow$$

Zirconium (IV) methanesulfonate from $ZrCl_4$,[4]

$$ZrCl_4 + 4\ MSA \rightarrow Zr(OMs)_4 + 4\ HCl(g)\uparrow \text{ (reaction run in anhydrous } CCl_4)$$

Sodium methanesulfonate from NaCl,[5]

$$NaCl + MSA \rightarrow NaOMs + HCl(g)\uparrow$$
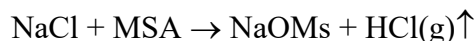
Chromium (III) methanesulfonate from $CrCl_3$,[6]

$CrCl_3$ + 3 MSA → $Cr(OMs)_3$ + 3 HCl(g)↑
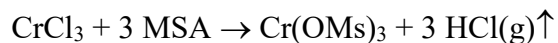
Thallium (III) methanesulfonate from $Tl(OAc)_3$,[7]

$Tl(OAc)_3$ + 3 MSA → $Tl(OMs)_3$ + 3 AcOH↑
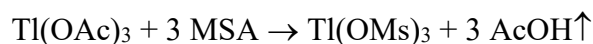
Cupric methanesulfonate from cupric benzoate,[8]

$Cu(OBz)2$ + 2 MSA → $Cu(OMs)_2$(s) + 2 BzOH
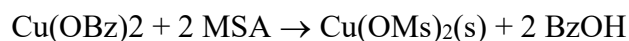
    The reaction of an acidic or neutral metal salt with MSA does not spontaneously give a high yield of metal methanesulfonate product. In general, this type of a reaction must be driven to completion. The reaction is most commonly driven forward by volatilization of the co-product acid through heating, the application of vacuum and/or the use of a continuous flow of sparging gas (typically nitrogen). Occasionally, the reaction is driven to completion through precipitation of the metal methanesulfonate. To promote volatilization of the co-product acid and/or precipitation of the metal methanesulfonate product, this type of reaction is normally run in an anhydrous medium. In some cases, a solvent that helps to expel the co-product acid (*e.g.*, CCl_4 or $CHCl_3$/EtOAc) is used. One advantage of this type of reaction is that the product is obtained in an anhydrous state. One disadvantage of this method is that generally the reaction can not be driven to 100% completion, and typically greater than 100 ppm of the reactant metal salt remains in the final metal methanesulfonate product. The metal methanesulfonate produced by this type of reaction is generally purified by washing with and/or recrystallization from a hydrophilic organic solvent. As a final purification step, the solid product is oftentimes heated under vacuum to remove all traces of water and/or wash/recrystallization solvent. The following procedures are illustrative:[1]

Silver Methanesulfonate, AgOMs: A 100 ml RBF was charged with $AgNO_3$ (17.25 g, 101 mmol) and 70% aqueous MSA (14.5 grams, 106 mmol). The flask was fitted with a condenser and a 100 ml ice cooled receiving flask. The reaction mixture was stirred and put under aspirator vacuum (14 mm Hg). The stirred reaction solution was gently heated to 90 °C over 1 hour and then kept at this temperature for several hours during which time most of the nitric acid distilled into the cooled collection flask. The remaining solid, still under vacuum, was further heated over one hour to an ultimate temperature of 170 °C. The flask was then cooled and the solid product removed. The crude product was washed with some acetone and ether to yield AgOMs with less than 100 ppm of residual nitrate. The yield of AgOMs was close to 100%. AgOMs, %Ag/% S (theoretical) = 3.36, %Ag/%S (actual) = 3.36, analysis by ICP/emission for %Ag and %S. Note that nitrate salts may be explosive, and while we encountered no trouble with this procedure, it is not generally recommended as the easiest way to produce AgOMs. We present it as an example.

Mercuric Methanesulfonate, $Hg(OMs)_2$: A mixture (1:2 molar) of $Hg(NO_3)_2$ and 70% MSA(aq) was heated under vacuum (30 mm Hg, teflon lined vacuum pump, caustic trap on pump outlet). The temperature of the stirred mixture was slowly raised from RT to about 100 °C over 1 h (do not let the temperature exceed 110 °C), and the heating was continued at 100 °C for several hours during which time most of the nitrate distilled off as nitric acid. The solid product had a nitrate level of less than 300 ppm. $Hg(OMs)_2$, %Hg/%S (theoretical) = 3.13, %Hg/%S (actual) = 3.12, analysis by ICP/emission for %Hg and %S. Though no tendency for energetic decomposition was noted, it is known that nitrate compounds can be unstable. As a precaution, the reaction apparatus was placed behind an explosion shield.

It has been found that the metal methanesulfonates produced by the reaction of metal chlorides and/or metal benzoates with MSA, as described above, are polymeric in nature.[6,8,9] However, it is not apparent to the casual user that the metal methanesulfonates produced via these techniques are any different than metal methanesulfonates produced by other methods. It has been shown that structural isomerism is possible in ferrous methanesulfonate, and the conversion of α-Fe(OMs)$_2$ to β-Fe(OMs)$_2$ can be accomplished by refluxing α-Fe(OMs)$_2$ for 3 days in 2,2-dimethoxypropane.[10,11] There is some similarity between the conditions required for the production of metal methanesulfonates from metal chlorides and the conditions required for the isomerism of α-Fe(OMs)$_2$ to β-Fe(OMs)$_2$ in that both methods require the use of elevated temperatures for an extended period of time, but no structural isomerism has been found in any metal methanesulfonate salt other than Fe(OMs)$_2$. Thus, despite the fact that separate CAS numbers have been assigned for polymeric forms of V(III), Cr(III), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) methanesulfonate, we can find no proof that these "polymeric" metal salts are any different from metal methanesulfonates containing the same metal cation but produced by alternative methods.
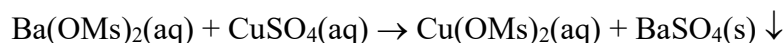
C) The metathesis of a IIA metal methanesulfonate with a soluble metal sulfate:

This method can be used to advantage in situations where it is necessary that a soluble metal sulfate starting material be employed (*e.g.*, commercial situations wherein a metal sulfate starting material is cheapest). Barium methanesulfonate is almost always employed for laboratory scale preparations, but strontium methanesulfonate and/or calcium methanesulfonate might also be employed. The general method is illustrated by the following reactions.

Cobalt (II) methanesulfonate from cobalt (II) sulfate,[12]

$$Ba(OMs)_2(aq) + CoSO_4(aq) \rightarrow Co(OMs)_2(aq) + BaSO_4(s)\downarrow$$
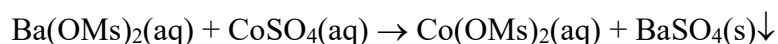
Cupric methanesulfonate from cupric sulfate,[13]

$$Ba(OMs)_2(aq) + CuSO_4(aq) \rightarrow Cu(OMs)_2(aq) + BaSO_4(s)\downarrow$$

This type of reaction is driven to completion by precipitation of the IIA metal sulfate co-product. In general, the reaction is run with stoichiometrically equivalent amounts of the IIA metal methanesulfonate and the soluble metal sulfate. The use of an excess of the IIA metal methanesulfonate will result in IIA metal methanesulfonate contamination in the product. Likewise, the use of excess soluble metal sulfate will result in metal sulfate contamination in the metal methanesulfonate product. Both excess IIA metal methanesulfonate and excess metal sulfate contamination are difficult to remove with standard purification techniques (*e.g.*, solvent washing, recrystallization), and generally the use of an excess of either reactant is not recommended. The following procedure represents one method of producing barium methanesulfonate for use as a starting material in sulfate/methanesulfonate metathesis reactions:[1]

Barium Methanesulfonate, Ba(OMs)$_2$: A 1 liter beaker was charged with 70% aqueous MSA (274 g, 2 moles) and powdered barium carbonate (197 g, 1 mole). The mixture was stirred and heated to 80 °C while an additional portion of 70% aqueous MSA (100 g, 36% excess) was slowly added. After one hour, enough DI H$_2$O was added to produce a homogeneous solution at 80 °C. A 50 ml dose of isopropyl alcohol was added, and the still clear solution was allowed to cool to room temperature over several hours during which time the product crystallized. The crystalline product was collected by vacuum filtration and washed with isopropyl alcohol and ether. The solid product was brought to constant weight *in-vacuo* (1 mm Hg). The yield of Ba(OMs)$_2$ was 72%. Ba(OMs)$_2$, %Ba/%S (theoretical) = 2.14, %Ba/%S (actual) = 2.16, analysis by ICP/emission for %Ba and %S.

The aqueous solubilities of some metal methanesulfonates, metal sulfates and metal chlorides are presented in Table 1. All the simple metal methanesulfonate salts are relatively soluble in aqueous solution being similar to metal nitrates and perchlorates in this respect. On the other hand, a number of metal sulfates have virtually no solubility in aqueous solution. The insoluble metal sulfates include strontium, barium, mercury (II) and lead (II) sulfate. In addition, calcium and silver sulfate have very low aqueous solubility.

Metal Cation	Aqueous Solubility (mol dm^{-1} as metal, 22 °C)		
	Methanesulfonate	Sulfate	Chloride
NH$_4^+$	6.83	8.17	5.06
Li$^+$	7.06	4.90	9.37
Na$^+$	5.65	2.78	5.57
K$^+$	4.48	1.25	3.86
Mg^{+2}	1.40	2.63	5.02
Ca^{+2}	2.92	0.02	5.51
Sr^{+2}	2.55	0.00	3.04
Ba^{+2}	1.59	0.00	1.71
Mn^{+2}	2.90	3.52	4.12
Co^{+2}	2.53	2.16	3.87
Ni^{+2}	2.13	2.44	4.38
Cu^{+2}	2.00	1.35	4.87
Ag$^+$	3.72	0.06	0.00
Zn^{+2}	2.16	3.32	13.00
Cd^{+2}	3.20	3.10	5.71
Sn^{+2}	3.73	1.42	4.91
Hg^{+2}	1.81	0.00	0.24
Pb^{+2}	2.60	0.00	0.03

Table 1: The saturation aqueous solubility of some metal methanesulfonates, metal sulfates and metal chlorides. The saturation solubilities are reported in units of molarity. All the data was measured at 22 °C. Saturation solubilities of less than 0.01 M are reported as 0.00 in the table. See the original reference for experimental details.[1]

In principle, one could use strontium, barium, mercuric or lead(II) methanesulfonate to carry out an efficient metathesis reaction with a soluble metal sulfate, but toxicity considerations contraindicate the use of mercury or lead. If some sulfate contamination is acceptable in the product, then calcium and/or silver methanesulfonate are also feasible starting materials for metal sulfate to methanesulfonate metathesis reactions. Of the two, calcium methanesulfonate is preferable to silver methanesulfonate both in terms of toxicity and completeness of reaction. The aqueous solubilities of the IIA metal sulfates along with some normalized toxicity data for salts of the corresponding IIA metal cations are shown below in Table 2.

IIA Metal Cation	Aqueous Solubility of IIA Sulfate[a]	Normalized Toxicity of IIA Cation[b]
Be(II)	42.4 (26 °C)	86 mg/kg[c]
Mg(II)	71.0 (20 °C)	2800 mg/kg[d], 3149 mg/kg[e]
Ca(II)	0.209 (30 °C)	3900 mg/kg[f]
Sr(II)	0.014 (30 °C)	2750 mg/kg[g]
Ba(II)	0.000246 (25 °C)	355 mg/kg[h]

Table 2: The aqueous solubility of the IIA metal sulfates compared with some normalized toxicity data for the corresponding IIA metal cations.

a)   Weast, R. C., Handbook of Chemistry and Physics, 68th Edition 1987-1988, CRC Press, Boca Raton, FL, B68-B146. Aqueous solubility measurements are in g salt per 100 g of water, temperature at which the solubility measurement was taken is parenthesis.
b)   LD50 values, ORL-RAT
c) $BeCl_2$: *Hygiene & Sanitation: English Translation of Gigiena Sanitariya* **1965**, *30(1-3)*, 169.
d) $MgCl_2$: *Journal of Pharmacology & Experimental Therapeutics* **1929**, *35*, 1.
e) $Mg(NO_3)_2$: *Sbornik Vysledkv Toxixologic Keho Vysetreni Latek A Pripravku* **1972**, 9.
f) $Ca(NO_3)_2$: *Sbornik Vysledkv Toxixologic Keho Vysetreni Latek A Pripravku* **1972**, 9.
g) $Sr(NO_3)_2$: *Gigiena Sanitariya* **1976**, *41(5)*, 28.
h) $Ba(NO_3)_2$: *Sbornik Vysledkv Toxixologic Keho Vysetreni Latek A Pripravku* **1972**, 10.

It can be seen from Table 2 that beryllium and magnesium methanesulfonate are not useful for sulfate to methanesulfonate metathesis reactions. Calcium, strontium and barium sulfate all have sufficiently low aqueous solubilities to allow for sulfate to methanesulfonate metathesis to occur when the corresponding methanesulfonate salts are reacted with a soluble metal sulfate. The extent of completion of the sulfate to methanesulfonate metathesis reaction increases in the order Ca^{+2}, Sr^{+2}, Ba^{+2}. However, the toxicity of soluble metal salts containing these cations also increases in the order Ca^{+2}, Sr^{+2}, Ba^{+2} (see Table 2 above). For laboratory scale preparations wherein material handling considerations are minimal and/or for cases where the metal methanesulfonate product must have an absolute minimum of sulfate content, the use of barium mesylate is indicated. For commercial scale preparations wherein a low level of sulfate contamination is acceptable, the use of calcium or strontium mesylate should be considered.
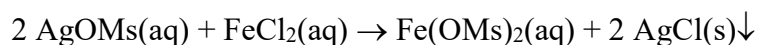
D) The metathesis of AgOMs with a soluble metal chloride, bromide or iodide:

This method can be used to advantage in situations where it is necessary that a soluble metal chloride starting material be employed (*e.g.*, commercial situations wherein a metal chloride starting material is cheapest). Silver methanesulfonate is always employed for this reaction. Some other metal methanesulfonate salts that might be used are lead (II) methanesulfonate and mercuric methanesulfonate, but both of these alternative salts are more toxic than AgOMs and the completeness of the corresponding reaction is less. Thus, silver mesylate is always indicated. The general method is illustrated by the following reactions.

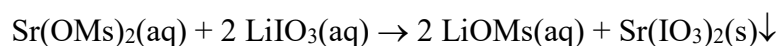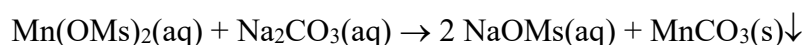Cesium methanesulfonate from cesium bromide,[14]

$$AgOMs(aq) + CsBr(aq) \rightarrow Cs(OMs)(aq) + AgBr(s)\downarrow$$
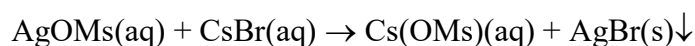
Ferrous methanesulfonate from ferrous chloride,[10]

$$2\ AgOMs(aq) + FeCl_2(aq) \rightarrow Fe(OMs)_2(aq) + 2\ AgCl(s)\downarrow$$

This type of reaction is driven to completion by precipitation of the silver halide co-product. The reaction is run with stoichiometrically equivalent amounts of silver methanesulfonate and the soluble metal chloride, bromide and/or iodide. The use of an excess of the silver methanesulfonate will result in silver contamination in the product. Likewise, the use of excess soluble metal chloride will result in chloride contamination in the product. Both silver methanesulfonate and excess metal chloride contamination are difficult to remove with standard purification techniques (*e.g.*, solvent washing, recrystallization), and the use of an excess of either reactant is not recommended. It should be noted that silver methanesulfonate based metathesis reactions will not work with soluble metal fluorides, as the aqueous solubility of silver fluoride is quite high. If for some reason it was necessary to use a soluble metal fluoride starting material, then a fairly efficient metathesis could be carried out with magnesium or calcium methanesulfonate (see standard tables of aqueous solubilities of metal salts for details).

Metal methanesulfonate preparations based on solubility driven anion/cation metathesis reactions other than those involving Ba^{+2} (method C) and Ag^+ (method D) are possible. For instance, sodium methanesulfonate can be prepared via the reaction of manganese methanesulfonate with sodium carbonate, and lithium methanesulfonate can be prepared via the reaction of strontium methanesulfonate with lithium iodate,

$$Mn(OMs)_2(aq) + Na_2CO_3(aq) \rightarrow 2\ NaOMs(aq) + MnCO_3(s)\downarrow$$

$$Sr(OMs)_2(aq) + 2\ LiIO_3(aq) \rightarrow 2\ LiOMs(aq) + Sr(IO_3)_2(s)\downarrow$$

Such alternative procedures are usually impractical in that they require less readily accessible starting materials and/or they convert more valuable salts into less valuable ones.

E) The exchange of ions with an insoluble (e.g., polymeric) resin:

When an aqueous solution of cupric methanesulfonate is passed at an appropriate rate through a column containing the sodium form of a cation exchange resin (*e.g.*, Amberlyst 36W) with a large overall excess of bound sodium ions relative to aqueous cupric ions, the cupric salt is quantitatively converted to the sodium salt.[3] The process is driven by statistical and chemical equilibration of the resin with the process stream. The overall process is relatively inefficient in that a large excess of the desired product cation must be present on the cation-exchange resin in order to obtain a pure cation-exchanged product.

$$M(OMs)_2 + Cation\text{-}Ex\ Resin\ (n\ M'^{+2}) \rightarrow M'(OMs)_2 + Cation\text{-}Ex\ Resin\ (n\text{-}1\ M'^{+2},\ M^{+2})$$
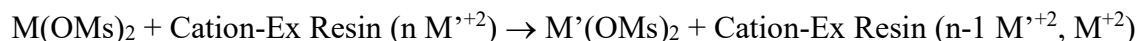
Cation-exchange resins are routinely used to remove low levels of soluble metal cations from aqueous effluents. Once such cation-exchange resins are completely loaded (cation-exchange sites are fully occupied by the metal cations being removed), they are commonly regenerated by conversion back to the protonic form. Passing an aqueous solution of an appropriate acid through the loaded resin carries out such conversion to the protonic form. The protons in the acid stream displace the metal cations from the resin's anionic sites. When a metal loaded resin has a significant amount of Pb^{+2}, Hg^{+2}, Ag^+ or Sn^{+2} on it, then MSA is oftentimes the best choice for regeneration acid. The ideality of MSA results from its ability to solubilize $Pb^{+2}(aq)$, $Hg^{+2}(aq)$, $Ag^+(aq)$ or $Sn^{+2}(aq)$, coupled with its nonoxidizing nature. The other acids that might be used (*e.g.*, HNO_3, $HClO_4$) for this purpose are more difficult to handle. As a result of the regeneration of a metal loaded cation-exchange resin, one obtains a concentrated aqueous solution of the discharged metals. When MSA is used as the regeneration acid, metal methanesulfonates are obtained in the regeneration byproduct stream. In some cases, the metal methanesulfonates formed by regeneration of a cation-exchange resin with MSA have been recycled back into an industrial process (*e.g.*, a Sn/Pb electroplating operation).[1] Beyond this, the cation-exchange method is of little importance in the practical manufacture of metal methanesulfonate salts.

Alternatively, an anion-exchange resin loaded with mesylate anions can be used to convert any aqueous soluble metal salt into a metal methanesulfonate. Again, the process is driven by statistical and chemical equilibration of the resin with the process stream.

$$MX_2 + \text{Anion-Ex Resin (n OMs}^-) \rightarrow M(OMs)_2 + \text{Anion-Ex Resin (n-2 OMs}^-, 2 X^-)$$

In practical operation, a very large excess of resin fixed methanesulfonate anions relative to process stream reactant anions must be present in order to obtain a pure metal methanesulfonate product, and once reactant anions start to break-through (appear in the column effluent) the resin must be regenerated. Regeneration of a partially exchanged resin will result in a regeneration byproduct stream that contains both the metal methanesulfonate salt used for regeneration and a byproduct salt, and the regeneration stream will not allow for a convenient recycle. Thus, the anion-exchange method of producing metal methanesulfonates will waste a good amount of the regeneration salt (*e.g.*, sodium methanesulfonate). Owing to the complexity of building continuous anion-exchange units and to the relatively poor efficiency and economics of such conversions, the anion-exchange method has not been found to be of practical value.

F) The chemical oxidation of elemental metal in methanesulfonic acid solution:

This method involves the chemically driven oxidation of elemental metal immersed in a solution of MSA. This method is sometimes the cheapest commercial route for the production of certain metal methanesulfonate. The general method is illustrated by the following reaction.

Silver methanesulfonate from elemental silver and hydrogen peroxide,[1,15]
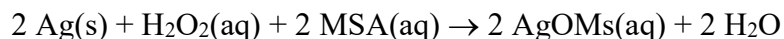
$$2\ Ag(s) + H_2O_2(aq) + 2\ MSA(aq) \rightarrow 2\ AgOMs(aq) + 2\ H_2O$$

This type of reaction is driven to completion by the release of the chemical potential associated with reduction of the oxidizing agent. The reaction is heterogeneous, and to obtain a reasonable reaction rate one must use metal with sufficiently high surface area. In the case of elemental silver, a fine powder works best. The use of an excess of MSA is generally employed. The final product can be isolated as a solid by evaporation of the solvent (water), and the product can be further purified by washing with a hydrophilic organic solvent or by recrystallization. When hydrogen peroxide is used as the oxidant, the intermediate formation of nascent metal oxide is likely. The following procedures are illustrative:[1]

Silver Methanesulfonate, AgOMs: Hydrogen peroxide (93 mmol, 2X excess) was added to a stirred mixture of silver metal (10 g, 93 mmol) in 20 ml of 70% MSA(aq) at such a rate that the temperature was kept below 45 °C. Following peroxide addition, the stirred solution was maintained at 35 °C for approximately 18 h. A drop of the solution was tested at regular intervals for unreacted H_2O_2 (I^-/starch). After all of the initial oxidant charge had been consumed (reaction time depends on the surface area of the silver used), an additional portion of hydrogen peroxide (93 mmol) was added as before. Following the complete consumption of the second portion of oxidant, the reaction mixture was vacuum filtered through a 1 micron glass fibre pad. The time-averaged rate of the reaction, under the conditions listed above, was about 1 mg Ag dissolution per hour per cm^2 of silver surface area. The higher the specific surface area (cm^2 per gram) of the metallic silver employed, the greater the rate of oxidative dissolution. With very fine silver powders (350 mesh and finer), the reaction required vigorous cooling and the total reaction time was on the order of several hours (note that reaction temperatures above 50 °C lead to excessive decomposition of the hydrogen peroxide). With silver powders of intermediate fineness (app. 100 mesh),

the reaction took about 18 h. With silver chunks cut from a slab, the reaction was too slow to be useful. The total consumption of the available silver was between 10% and 100% (finer powders allow for higher total consumption). The reaction yield was always 100% relative to the silver consumed. The reaction yield was between 10% and 45% relative to the hydrogen peroxide consumed. The final product was obtained by evaporating the reaction filtrate down to a crude solid, washing the crude solid with solvent (acetone and ether) and drying the washed solid to constant weight *in-vacuo* (1 mm Hg). The purity of AgOMs produced with this method was 99%+.

Palladium Methanesulfonate, Pd(OMs)$_2$: In a 50 ml beaker, 350 mesh palladium powder (1.06 g, 10 mmol), 70% aqueous MSA (2.72 g, 2 ml, 20 mmol) and conc. aqueous HNO$_3$ (1.4 g, 1 ml, 16 mmol) were mixed. The reaction was initiated by the addition of one drop of conc. HCl(aq). The stirred suspension rapidly turned dark brown, and the reaction was complete within 30 minutes. The solution was diluted to [Pd] = 5 g/l and used as is.

G) The anodic dissolution of elemental metal in methanesulfonic acid solution:

This method involves the anodically driven oxidation of elemental metal immersed in a solution of MSA. This method is usually the cheapest commercial route for the production of large amounts of certain metal methanesulfonate. The general method is illustrated by the following reactions.
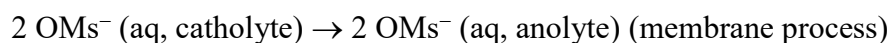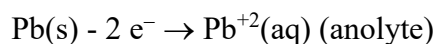
Silver methanesulfonate by the anodic oxidation of silver in MSA(aq),[1]

Ag(s) - 1 e$^-$ → Ag$^+$ (aq) (anode)

HOMs(aq) + 1 e$^-$ → OMs$^-$ (aq) + ½ H$_2$(g)↑ (cathode)
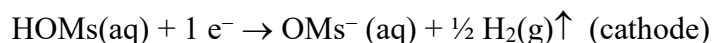
Lead (II) methanesulfonate by the anodic oxidation of lead in MSA(aq),[16,17]

Pb(s) - 2 e$^-$ → Pb^{+2} (aq) (anode)

2 HOMs(aq) + 2 e$^-$ → 2 OMs$^-$ (aq) + H$_2$(g)↑ (cathode)

This type of reaction is driven by the application of electrochemical potential. The reaction is heterogeneous, but normally a good reaction rate can be obtained with simple (*i.e.*, low surface area) slabs of metal. The use of an excess of MSA is generally employed. Again, the final product can be isolated as a solid by evaporation of the solvent (water), and then the solid can be further purified by washing with a hydrophilic organic solvent or by recrystallization. In order to improve the efficiency of the process, some accommodation must be made to keep the reducible metal cation that is being formed away from the cathode. This can be done conveniently by separating the cell into an anolyte and catholyte chamber with an anion-exchange membrane. The metal anode dissolves into the anolyte while MSA is reduced to methanesulfonate and hydrogen in the catholyte. The anion-exchange membrane allows for transport of methanesulfonate from the catholyte into the anolyte, but it prevents the transport of metal cations from the anolyte into the catholyte. The overall process is shown below:

Pb(s) - 2 e$^-$ → Pb^{+2}(aq) (anolyte)

2 HOMs(aq) + 2 e$^-$ → 2 OMs$^-$ (aq) + H$_2$(g)↑ (catholyte)

2 OMs$^-$ (aq, catholyte) → 2 OMs$^-$ (aq, anolyte) (membrane process)

As an alternative to the use of an anion-exchange membrane, a vertical arrangement of a lower anode and an upper cathode in an undivided flow through cell can sometimes be used. This type of cell, oftentimes referred to as a "gravitationally separated cell", employs a slow and continuous flow of electrolyte through the cell from top to bottom. The product salt is formed on the lower anode, and the top-down flow of electrolyte inhibits the migration of the reducible metal cations upward toward the cathode. Oftentimes in this type of cell, a visibly distinct and segregated thick lower layer of metal methanesulfonate solution forms around the anode. Such visibly distinct layers of metal methanesulfonate solution can be used to conveniently adjust the flow rate of electrolyte through the cell. The electrolyte flow rate is set such that the visible lower anode layer remains in the lower half of the cell. However, even with careful adjustment of the flow rate, there is almost always some reduction of dissolved metal cations to metal (usually to a fine metal powder) on the cathode. The basic principles of electrochemistry and ion-exchange membranes are outlined in a number of excellent books.[18,19] The following procedure is illustrative,

Silver Methanesulfonate, AgOMs: An anion-exchange membrane (50 cm^2, ESC-7001, available from the Electrosynthesis Company, Lancaster, NY) divided electrochemical tank cell with a 1 liter anolyte and 1 liter catholyte compartment was fitted with a 60 cm^2 (one side) Ag anode and a 60 cm^2 (one side) Ni cathode (inter-electrode distance = 6 cm). The anolyte chamber was charged with 1 Kg of 2% MSA(aq), and the catholyte chamber was charged with 1 liter of 250 g/l MSA(aq). The main anode process was oxidative silver dissolution, and the main cathode process was hydrogen formation. The main membrane process was methanesulfonate transfer from the catholyte to the anolyte. A current of 4 A (cell voltage = 5 V) was passed for 6 hours, and then a current of 1 A (cell voltage = 3 V) was passed for 14 hours. The temperature of the electrolyte increased over the initial 2 h to a final steady value of 33 °C. The conductivity of the cell decreased as MSA was consumed in the catholyte, and occasional MSA additions to the catholyte were made. After 20 hours, the anolyte was removed and evaporated down to a solid. The solid was washed with a small amount of solvent (acetone and ether) and reduced *in-vacuo* to constant weight. The final weight of AgOMs was 218 g (76% current efficiency). The product purity was 99% plus.

H) The steeping of active metals in methanesulfonic acid solution:

This method involves the chemically driven oxidation of elemental metal immersed in a solution of MSA, wherein the chemical oxidant is a proton. This method is sometimes the cheapest commercial route for the production of some metal methanesulfonates. The general method is illustrated by the following reaction.

Ferrous methanesulfonate from iron powder in MSA(aq),[1]
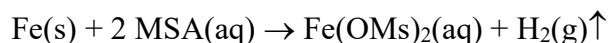
$$Fe(s) + 2\ MSA(aq) \rightarrow Fe(OMs)_2(aq) + H_2(g)\uparrow$$

This type of reaction is driven to completion by the release of the chemical potential associated with the reduction of a proton. The reaction is heterogeneous, and to obtain a reasonable reaction rate one must use metal with sufficiently high surface area. For most metals, a fine powder (60+ mesh) works best. The use of an excess of MSA is generally employed. Because the proton is not a strong oxidizing agent, this reaction is limited to more active metals (*i.e.*, metals whose corresponding cation has an E^o more negative than -0.1 V). Accommodation must be made for the venting of the hydrogen gas formed, and with active metal powders the rate of hydrogen gas formation can be problematic. The final product can be isolated as a solid by evaporation of the solvent (water), and then the solid can be further purified by washing with a hydrophilic organic solvent or by recrystallization. The following procedure is illustrative:[1]

Ferrous Methanesulfonate, Fe(OMs)$_2$: A 4 liter beaker was charged with 1.5 Kg of 70% aqueous MSA (10.9 moles). To the well stirred MSA(aq) was added 250 grams of iron powder (4.5 mol, 10 micron 99.9%) in small portions over 6 h (insure adequate ventilation to remove the H$_2$ gas formed). After all the iron had been added, the solution was stirred at RT for an additional 14 hours. Finally, the solution was filtered through a 1 micron glass microfibre pad and analyzed for [Fe] and free acid. A solution with [Fe] = 67.2 g/l and free acidity = 0.50 M was obtained.

I) The chemical conversion of the anionic portion of a related metal salt:

This method involves the chemical conversion of a related metal salt into a metal methanesulfonate salt. In the specific case of metal methanesulfonates, this type of chemical conversion almost always involves oxidation. This method has been proposed as an economical alternative route for the production of certain metal methanesulfonates. The general method is illustrated by the following reaction.

Lead methanesulfonate from lead methanethiolate,[1]

$$Pb(SMe)_2(s) + 3\ O_2 \rightarrow Pb(OMs)_2(aq)\ \text{(nitric acid catalysis)}$$
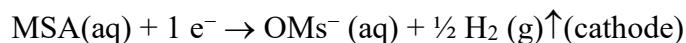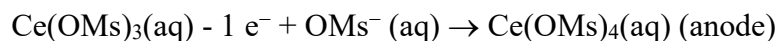
The methanethiolate ligands are oxidized directly to methanesulfonate.

J) The REDOX conversion of a metal methanesulfonate salt:

This method involves the oxidation or reduction of a metal ion. This method has been used for the economical *in-situ* production of a more energetic oxidation state of a metal within a metal methanesulfonate salt. The general method is illustrated by the following reaction.

Cerric methanesulfonate by anodic oxidation of cerrous methanesulfonate,

$$Ce(OMs)_3(aq) - 1\ e^- + OMs^-\ (aq) \rightarrow Ce(OMs)_4(aq)\ \text{(anode)}$$

$$MSA(aq) + 1\ e^- \rightarrow OMs^-\ (aq) + \tfrac{1}{2}\ H_2\ (g)\uparrow\text{(cathode)}$$

This type of reaction is driven by the application of chemical potential (i.e., strongly oxidizing or reducing reagents, anodic or cathodic current). As this method is normally used for the *in-situ* production of an energetic oxidation state of a particular metal methanesulfonate, it normally is not associated with a purification routine. For completeness, one must recognize that certain metal methanesulfonates might also be produced by the reduction of existing metal methanesulfonate salts (e.g., ferrous mesylate via the cathodic reduction of ferric mesylate).

Summary of Preparative Methods:

The nine methods (A - I) employed for the preparation of metal methanesulfonates can be combined into three general reaction types:

1)   Anion/Cation Metathesis (A - E)

2)   Direct REDOX Conversion of Elemental or Ionic Metal (F - H, J)

3)   Chemical Conversion (I)

Anion/cation metathesis reactions are driven forward by favorable changes in pH (method A), by removal *in-vacuo* of the protonated form of the undesired anion (method B), by concentration driven metathesis (method E) or by solubility driven removal of a byproduct salt containing the undesired anion (methods B, C, D). Direct oxidative methods are distinct in that they allow for the direct introduction of the desired metal cation into a solution containing the requisite amount of methanesulfonate counter anions (methods F, G, H, J). Finally, chemical conversion methods allow for the preparation of metal methanesulfonates through the chemical transformation, by any known means, of the anion of some related metal salt (method I).

Comprehensive Review of Metal Methanesulfonate Preparations:

A full review of those methods that have been previously employed to prepare various metal methanesulfonate salts is given below in Table 3. Table 3 is comprehensive for all known anhydrous and hydrated metal methanesulfonate compounds. The preparative references cited include all those that describe in detail the preparation of one or more metal methanesulfonate compounds. In cases where the hydration state of the metal methanesulfonate was not determined or implied, the anhydrous state is indicated. In addition, we have included in Table 3 a number of entries for simple metal methanesulfonate solvates, but this listing is representative as opposed to comprehensive. Note that this survey only includes compounds that have a number of methanesulfonate anions equivalent to the total cationic charge of the metal(s).

Alkali & Alkaline Earth Metal Methanesulfonates				
Cation[a]	Hydrate[b]	Solvate[c]	CAS #[d]	Preparative Methods and References[e]
Li^+	-	-	2550-62-1	A[1,20,21,22,23], C[22,24]
$^6Li^+$	-	-	20666-96-0	A[25]
$^7Li^+$	-	-	20666-97-1	A[25]
Na^+	-	-	2386-57-4	A[2,20,21,22,25,26,27,28,29,30,31,32,33], B[5], C[22]
K^+	-	-	2386-56-3	A[1,20,21,22], C[22,24]
Rb^+	-	-	84238-86-8	A[20]
Cs^+	-	-	2550-61-0	A[2,20,34,35], B[36], D[14]
Mg^{+2}	-	-	62512-10-1	A[1,36], C[24]
Ca^{+2}	-	-	58131-47-8	A[1,24,38,39]
Sr^{+2}	-	-		A[1,24]
Ba^{+2}	-	-	26755-96-4	A[1,24,40,41]

Transition Metal Methanesulfonates				
Cation[a]	Hydrate[b]	Solvate[c]	CAS #[d]	Preparative Methods and References[e]
Ti^{+3}	-	-	89702-94-3	NI
Ti^{+4}	-	-	55042-25-6	B[42]
Ti^{+4}	-	2 Py		B[42]
Ti^{+4}	-	2 $BuNH_2$		B[42]
V^{+3}	-	-	55136-32-8	B[6]
V^{+3}	-	-	55136-33-9	HP, B[6]
V^{+3}	-	3 Py		B[9]
V^{+3}	-	Bipy		B[9]
V^{+3}	-	2 Bipy		B[9]
Cr^{+2}	-	-	57518-93-1	B[23,43,44]
Cr^{+3}	-	-	55136-34-0	B[6], C[41]
Cr^{+3}	-	-	55136-35-1	HP, B[6]
Cr^{+3}	-	3 Py		B[9]
Cr^{+3}	-	Bipy		B[9]
Cr^{+3}	-	2 Bipy		B[9]
Mn^{+2}	-	-	88576-27-6	A[1,45], B[9]
Mn^{+2}	2	-	31177-94-3	C[46,47]
Mn^{+2}	4	-	30349-62-3	A[45]
Mn^{+2}	-	4 Py		A[45], B[9]
Mn^{+2}	-	2 Bipy		B[9]
Fe^{+2}	-	-	56525-23-6[f]	B[9,44,48], D[10,11], G[1]
Fe^{+2}	-	MSA	77214-81-4	D[10]
Fe^{+2}	-	4 Py		B[9]
Fe^{+2}	-	2 Bipy		B[9]
Fe^{+3}	-	-	59640-42-5	D[10]
Co^{+2}	-	-	55136-36-2	B[6], C[8,12]
Co^{+2}	-	-	55136-37-3	HP, B[6], C[8]
Co^{+2}	2	-	50910-89-9	A[1], C[12]
Co^{+2}	3	-		C[12]
Co^{+2}	4	-	114068-82-5	A[49,50], C[12]
Co^{+2}	5	-	50910-88-8	C[12]
Co^{+2}	7	-	50910-74-2	C[12]
Ni^{+2}	-	-	55136-38-4	A[1], B[6]
Ni^{+2}	-	-	55136-39-5	HP, B[6]
Cu^{+1}	-	-	91884-96-7	A[51], F[52]
Cu^{+2}	-	-	54253-62-2	A[1], B[6,8], C[24]
Cu^{+2}	-	-	55136-40-8	HP, B[6,8]
Cu^{+2}	4	-	25321-64-6	A[50,53], C[13,46]
Zn^{+2}	-	-	33684-80-9	A[1,37,54], B[36]
Zn^{+2}	4	-	56858-68-5	A[50,53], C[46]
Zn^{+2}	-	2 Py		B[36]

Cation	Hydrate	Solvate	CAS #	Preparative Methods and References
Zn^{+2}	-	2 $BuNH_2$		B[36]
Y^{+3}	-	-	77998-32-4	A[55]
Y^{+3}	3	-	73640-21-8	A[56]
Zr^{+4}	-	-	184420-73-3	B[4]
Mo^{+2}	-	-	64784-75-4	B[57]
Mo^{+2}	-	2 DMF		B[57]
Mo^{+2}	-	2 (-BL		B[57]
Pd^{+2}	-	-	74109-53-8	B[58], F[1]
Ag^{+1}	-	-	2386-52-9	A[1,14,24,39,46,59,60,61,62], B[63], F[1,15], G[1,64]
Ag^{+1}	-	2 P(Ph)$_3$		B[63]
Cd^{+2}	-	-	74440-47-4	A[1], B[65]
Cd^{+2}	2	-	56003-35-1	C[46,47]
Cd^{+2}	-	2 Py		B[65]
Cd^{+2}	-	3 Py		B[65]
Cd^{+2}	-	2 Quin		B[65]
Cd^{+2}	-	HQuin		B[65]
Cd^{+2}	-	2 HQuin		B[65]
Cd^{+2}	-	Bipy		B[65]
Cd^{+2}	-	2 Bipy		B[65]
Cd^{+2}	-	2 β-Pic		B[65]
Cd^{+2}	-	DMF		B[65]
Cd^{+2}	-	TMU		B[65]
Cd^{+2}	-	DMSO		B[65]
Au^{+1}	-	P(C_6C_{11})$_3$		D[63]
Hg^{+2}	-	-	54253-64-4	B[1]

Main Group Metal Methanesulfonates				
Cation[a]	Hydrate[b]	Solvate[c]	CAS #[d]	Preparative Methods and References[e]
Al^{+3}	-	-	91812-77-0	NI
In^{+3}	-	-	125923-01-5	G[66]
Sn^{+2}	-	-	53408-94-9	A[1], B[36], G[66]
Sb^{+3}	-	-	110917-98-1	A[34]
Sb^{+3}	-	2 Py		A[34]
Sb^{+3}	-	2 DMF		A[34]
Sb^{+3}	-	BBr_3		A[34]
Tl^{+1}	-	-	111962-27-7	NI
Tl^{+3}	-	-	54253-63-3	B[7]
Pb^{+2}	-	-	17570-76-2	A[1,24], G[16,17], I[1]
Bi^{+3}	-	-	82617-81-0	A[34]
Bi^{+3}	-	2 Py		A[34]
Bi^{+3}	-	2 DMF		A[34]
Bi^{+3}	-	BBr_3		A[34]

Lanthanide Methanesulfonates				
Cation[a]	Hydrate[b]	Solvate[c]	CAS #[d]	Preparative Methods and References[e]
La^{+3}	-	-	77998-19-7	A[55]
La^{+3}	2	-	73640-08-1	A[56]
Ce^{+3}	-	-	77998-20-0	A[55]
Ce^{+3}	2	-	73640-09-2	A[56,67]
Ce^{+4}	-	-	107355-42-0	J[68,69,70,71]
Pr^{+3}	-	-	77998-21-1	A[55]
Pr^{+3}	2	-	73640-10-5	A[56]
Nd^{+3}	-	-	77998-22-2	A[55]
Nd^{+3}	3	-	73640-11-6	A[56]
Sm^{+3}	-	-	77998-23-3	A[55]
Sm^{+3}	3	-	73640-12-7	A[56,67]
Eu^{+3}	-	-	78007-08-6	A[55]
Eu^{+3}	3	-	73640-13-8	A[56]
Gd^{+3}	-	-	77998-24-4	A[55]
Gd^{+3}	3	-	73640-14-9	A[56]
Tb^{+3}	-	-	77998-25-5	A[55]
Tb^{+3}	3	-	73640-15-0	A[56,67]
Dy^{+3}	-	-	77998-26-6	A[55]
Dy^{+3}	3	-	73640-16-1	A[56]
Ho^{+3}	-	-	77998-27-7	A[55]
Ho^{+3}	3	-	73640-17-2	A[56]
Er^{+3}	-	-	77998-28-8	A[55]
Er^{+3}	3	-	73640-18-3	A[56]
Tm^{+3}	-	-	77998-29-9	A[55]
Tm^{+3}	3	-	73640-19-4	A[56]
Yb^{+3}	-	-	77998-30-2	A[55,67]
Yb^{+3}	3	-	73640-22-9	A[56]
Lu^{+3}	-	-	77998-31-3	A[55]
Lu^{+3}	3	-	73640-20-7	A[56]

Mixed Metal Methanesulfonates				
Cations[a]	Hydrate[b]	Solvate[c]	CAS #[d]	Preparative Methods and References[e]
Li^+, Al^{+3}	-	-	105698-69-9	B[72] (from $LiAlCl_4$)
Cs^+, As^{+3}	-	-		A[34] (from $As(OMs)_3$ & CsOMs)
Cs^+, Sb^{+3}	-	-	110917-99-2	A[34] (from $Sb(OMs)_3$ & CsOMs)
Cs^+, Bi^{+3}	-	-	110918-00-8	A[34] (from $Bi(OMs)_3$ & CsOMs)
Na^+, Bi^{+3}	-	-	110917-97-0	A[34] (from $NaBiO_3$ & MsOMs)

Table 3: CAS numbers, preparative methods and representative references for a number of metal methanesulfonates.

a)   This column lists the metal cation(s) of the metal methanesulfonate compound.
b)   This column lists the number of waters of hydration.
c)   This column lists the number of and nature of any neutral solvating ligands. These metal methanesulfonate solvate compounds were nearly always prepared by the simple addition of an appropriate amount of a neutral solvating ligand to a solution of the uncomplexed metal methanesulfonate. Py = pyridine, $BuNH_2$ = *n*-butyl amine, Bipy = 2,2'-bipyridine, MSA = methanesulfonic acid, DMF = N,N-dimethylformamide, (-BL = (-butyrolactone, $P(Ph)_3$ = triphenylphosphine, Quin = quinoline, HQuin = 8-hydroxyquinoline, ∃-Pic = 3-methylpyridine (3-picoline), TMU = tetramethylurea, DMSO = dimethylsulfoxide, $P(C_6C_{11})_3$ = tricyclohexylphosphine, BBr_3 = boron tribromide.
d)   This column lists the CAS #, if one is available, for the compound.
e)   This column lists the generic methods used to prepare a particular metal methanesulfonate (A through G as described in the immediately previous section of this paper). Associated with each preparative method designation (A through G) is a list of references (superscript) that employed said method to make said compound. All reference numbers refer to the bibliography. HP designates a reference that claims that the metal methanesulfonate listed is polymeric in nature. We have found no evidence to suggest that such metal methanesulfonates are different from metal methanesulfonates containing the same metal cation but prepared by other methods. For completeness, we have included the CAS # information for the "polymeric" compounds. NI (not isolate) indicates that a preparative reference wherein the metal salt under consideration was isolated or otherwise proven to exist could not be found. The preparative methods listed (A through G) for solvate compounds designate the methods used to prepare the uncomplexed metal methanesulfonate.
f)   Note that references 10 and 11 give a procedure, basically an extended reflux in 2,2-dimethoxypropane, whereby an α structural isomer of ferrous methanesulfonate can be converted to a β structural isomer.

Stoichiometric Preparative Procedures that Employ Metal Methanesulfonates:

The stoichiometric chemical reactions of metal methanesulfonates can be divided into three general categories:

A)   Reactions wherein a metal methanesulfonate is used to introduce a mesyloxy group

B)   Reactions wherein a metal methanesulfonate is a starting material

C)   Reactions wherein a metal methanesulfonate has high solubility in the reaction solvent

The reactions wherein a metal methanesulfonate is used to introduce a mesyloxy group can be further subdivided into those reactions that involve silver methanesulfonate and those that don't involve silver methanesulfonate. The other two categories of reactions, those that involve the use of metal methanesulfonates as starting materials and those that require metal methanesulfonates for solubility reasons, do not require any further subdivision. First, we will review reactions that employ silver methanesulfonate to introduce a mesyloxy group.

*Reactions that employ silver methanesulfonate to introduce a mesyloxy group:*

a)   *Anion Exchange of Methanesulfonate for Halide in Organometallic Complexes:*

Titanocene dichloride has been converted to titanocene dimesylate via treatment with AgOMs,[73]

$$(Cp)_2TiCl_2 + 2\ AgOMs \rightarrow (Cp)_2Ti(OMs)_2 + 2\ AgCl(s)\downarrow$$
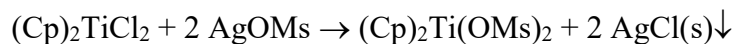
        A stirred mixture of 3.00 g of dichloro(dicyclopentadienyl)titanium, 5.25 g of silver methanesulfonate and 225 ml of THF was heated slowly to boiling and was gently boiled for 5 min. The hot mixture was filtered, and hexane was added to the filtrate. The resulting orange-red crystals were filtered, washed with hexane and dried at 25 °C and 0.1 mm Hg vacuum to give 2.65 g of dicyclopentadienylbis(methanesulfonato)titanium (60% yield). The product had a decomposition temperature of 170 °C. This and other titanocene complexes were tested as agents for increasing crop yields.

Zirconocene dichloride has been converted to zirconocene dimesylate via treatment with AgOMs,[74]

$$(Cp)_2ZrCl_2 + 2\ AgOMs \rightarrow (Cp)_2Zr(OMs)_2 + 2\ AgCl(s)\downarrow$$
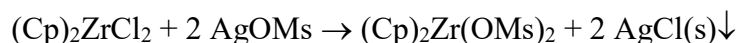
        Into a 300 ml glass reactor thoroughly purged with $N_2(g)$ were charged 100 ml of dry acetonitrile and 1.24 g (4.25 mmol) of zirconocene dichloride, and they were stirred at RT to give a homogeneous solution. To the mixed solution was added 50 ml of an acetonitrile solution containing 1.74 g (8.57 mmol) of silver methanesulfonate at RT over a period of 10 min, and the reaction was continued at RT for 2 hours. The produced salt was filtered over a glass filter in a stream of $N_2(g)$, and the obtained filtrate was concentrated *in-vacuo*. The solid obtained was recrystallized from toluene to yield 1.04 g of a colorless needle-like crystal (60% yield, mp 145-148 °C). This and other zirconocene complexes were tested as catalysts for olefin polymerization.

b)   *Anion Exchange of Methanesulfonate for Halide in Onium Compounds:*

Perfluoroalkyl 4-tolueneliodonium chlorides have been converted to the corresponding mesylates,[75]

$$ArIR_f\text{-}Cl + AgOMs \rightarrow ArIR_f\text{-}OMs + AgCl(s)\downarrow \qquad R_f = \text{perfluoroalkyl group}$$

Pyridinium chlorides and iodides have been converted to the corresponding mesylates,[76]

$$(PyCH_2OCH_2Py')Cl_2 + 2\ AgOMs \rightarrow (PyCH_2OCH_2Py')(OMs)_2 + 2\ AgCl(s)\downarrow$$
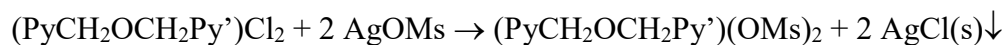
        Equimolar amounts of HI 6 dichloride (1-(4-aminocarbonylpyridino)methoxy)-methyl)-2-(hydroxyiminomethyl) pyridinium dichloride monohydrate) and silver methanesulfonate dissolved in 120 ml of 20% v/v aqueous MeOH containing 1 drop of MSA were mixed with stirring. The precipitated AgCl was suction filtered and washed with the above solvent. The collected filtrate was reduced to 20 ml *in-vacuo* at a temperature not exceeding 30 °C. Upon addition of ethanol (150-200 ml), HI 6 dimethanesulfonate crystallized. The crystals were dissolved in 10 ml of water at ambient temperature and recrystallized by the addition of 150 ml of ethanol (completion of crystallization at -20 °C). The white crystals (8.4 mmol, 61%) melted at 175-177 °C (decomp.). The product was used as an aqueous soluble antidote for organophosphate nerve gas.

c)   *Anion Exchange of Methanesulfonate for Bromide in Selenium Compounds:*

Diphenylselenium dihalides have been converted to the corresponding dimesylates,[77]

$$(Ph)_2SeBr_2 + 2\ AgOMs \rightarrow (Ph)_2Se(OMs)_2 + 2\ AgBr(s)\downarrow$$
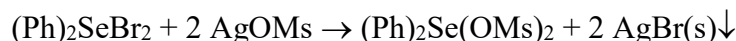
A number of tetra-coordinate diphenylseleniumdiol diesters (*e.g.*, sulfonate diesters) were produced. Some physical and spectral properties of the compounds were measured.

d)   *Anion Exchange of Methanesulfonate for Iodide in Organosilicon Compounds:*

Hindered organosilyl iodides have been converted to the corresponding mesylates,[78]

$$(Me_3Si)_3CSiPhHI + AgOMs \rightarrow (Me_3Si)_3CSiPhHOMs + AgI(s)\downarrow$$
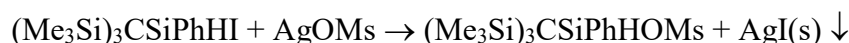
A mixture of tris(trimethylsilyl)methyl, phenyl, iodosilane (TsiSiPhHI, 0.46 g, 0.99 mmol) and AgOMs (0.22 g, 1.08 mmol) in ether (15 ml) was warmed in an open vessel until all the ether had evaporated. The residue was kept at 90 °C for 90 min and then cooled and extracted with pentane. The extract was filtered and evaporated and the residue sublimed to give TsiSiPhH(OMs) (0.40 g, 93%), mp 123-124 °C. Some spectral properties of this and related compounds were measured.

e)   *Formation of Mixed Acid Anhydrides from Acid Halides:*

Mixed sulfonic acid anhydrides have been prepared from alkanesulfonyl and arenesulfonyl chlorides and AgOMs,[79]

$$PhSO_2Cl + AgOMs \rightarrow PhSO_2OMs + AgCl(s)\downarrow$$
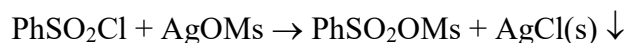
Benzenesulfonyl chloride (1.76 g, 10 mmol) and AgOMs (2.03 g, 10 mmol) were combined in 15 ml of CH_2Cl_2. The mixture was stirred for three days and then filtered to remove AgCl. The filtrate was evaporated to dryness, giving 1.45 g of a viscous liquid product. This and related mixed anhydrides of methanesulfonic acid were used as performance enhancing additives in peroxygen bleaches.

Mixed sulfonic perfluorosulfonic acid anhydrides have been prepared from perfluorosulfonyl chlorides and AgOMs,[80]

$$CF_3SO_2Cl + AgOMs \rightarrow CF_3SO_2OMs + AgCl(s)\downarrow$$
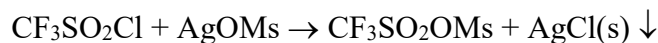
The mixed anhydride was prepared for use as an electrophilic mesylating agent.

Mixed sulfonic carboxylic acid anhydrides have been prepared from carboxoyl chlorides and AgOMs,[81,82]

$$PhCOCl + AgOMs \rightarrow PhCOOMs + AgCl(s)\downarrow$$
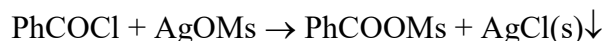
To a 500 ml Morton flask equipped with an overhead air-driven stirrer, was added 100 ml of acetonitrile (previously distilled from P_2O_5) and 20.2 g of AgOMs (0.1 mol). Isophthaloyl dichloride (10.15 g, 0.05 mol) dissolved in 10 ml of acetonitrile was slowly added to the stirred solution of AgOMs that was maintained below 20 °C with external cooling. After 16 h at RT, the AgCl was removed by filtration. The filtrate was evaporated to dryness, giving a solid residue with mp 133-135 °C. The residue

was dissolved in 500 ml of boiling benzene, and then filtered to remove a small amount of remaining silver salt. The filtrate on cooling gave 13.9 g (86% yield) of fine white needles with mp 132-135 °C. This and other mixed sulfonic carboxylic acid anhydrides were prepared as additives for bleach compositions.[81] In some related work, a number of other mixed sulfonic carboxylic acid anhydrides were prepared via similar procedures for general physical studies.[82]

Mixed sulfonic sulfenic acid anhydrides have been prepared from sulfenyl halides and AgOMs,[83]

$$PhSCl + AgOMs \rightarrow PhSOMs + AgCl(s) \downarrow$$
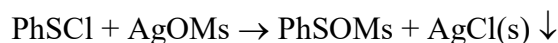
Mixed sulfonic phosphorous acid anhydrides have been prepared from phosphoroyl chlorides and AgOMs,[84]

$$(MeO)_2PCl + AgOMs \rightarrow (MeO)_2POMs + AgCl(s) \downarrow$$
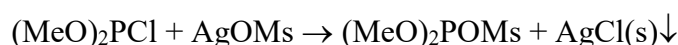
These compounds were prepared for hydrolysis studies. The use of mixed sulfonic phosphorous acid anhydrides as additives in perborate bleaches has been published.

f)   Formation of O-Glycosides from Sugars and Alcohols:

Sugars have been converted to O-glycosides via a reagent combination that includes Ph_2SiCl_2 and AgOMs,[85]

$$\alpha GOH + MeOH + Ph_2SiCl_2 + 2\ AgOMs \rightarrow \alpha GOMe + 1/n\ \{Ph_2SiO\}_n + 2\ AgCl(s) \downarrow + 2\ MSA$$

αGOH = tetra-O-benzylglucopyranose

AgOMs was used as a means of converting HCl to MSA *in-situ*. The HCl byproduct of the glycosidation reaction was found to be deleterious, and conversion of the HCl to AgCl improved the reaction yield and the product purity. In a similar procedure, 2,3,4,6-tetra-O-acetyl-1-O-mesyl-α-D-glucopyranose was prepared from the corresponding 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide by reaction with AgOMs in dry benzene under ice cooling.[86] The 2,3,4,6-tetra-O-acetyl-1-O-mesyl-α-D-glucopyranose was treated with various alcohols to yield O-glycoside ethers. Sugar-O-glycoside ethers are important synthetic intermediates.

g)   Formation of Alkyl, Allyl and Benzyl Methanesulfonates from Corresponding Halides:

Primary alkyl halides have been converted to the corresponding alkyl mesylates,[87,88,89]

$$RX + AgOMs \rightarrow ROMs + AgX(s) \downarrow$$
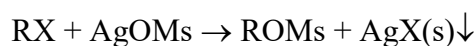
A variety of polar solvents can be employed (*e.g.*, acetonitrile, sulfolane, CH_2Cl_2), and the reaction can be run both homogeneously and heterogeneously in suspension. Generally, the reaction is heated to a temperature of approximately 60 °C or higher for a period of hours to days. The AgX byproduct is filtered off, and the product is purified by traditional means. The following procedure is illustrative:[88]

1,11-Undecanediol dimethanesulfonate: To a hot stirred solution of AgOMs (3.91 g, 19.3 mmol) in acetonitrile (25 ml) was added 1,11-dibromoundecane (3.0 g, 9.55 mmol). After heating under reflux in the dark for 20 h, the mixture was cooled, filtered and reduced to a solid residue *in-vacuo*. The residue

was extracted with hot 1,2-dichlorethane, filtered and the solvent evaporated to afford a white solid (2.82 g, 86%) - recrystallized from ethanol (mp 64-65 °C).

Allyl and benzyl bromides have been converted to allyl and benzyl mesylates,[90,91,92]

$$PhCH_2Br + AgOMs \rightarrow PhCH_2OMs + AgBr(s) \downarrow$$
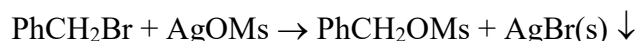
Acetonitrile is generally used as the solvent, and the reaction is typically run at room temperature for several hours. The AgBr byproduct is filtered from the desired reaction product that can then be purified by traditional means.[90,91] The following procedure is illustrative:

6-((Methanesulfonyloxy)methyl)-1,4-naphthoquinone: A mixture of 6-bromomethyl-1,4-naphthoquinone (1.5 g, 6 mmol) and silver methanesulfonate (4.8 g, 24 mmol) in acetonitrile (30 ml) was stirred at RT for 6 h. The solvent was removed in-vacuo at 40 °C, and the residue was extracted with CHCl_3 (5 X 50 ml). The combined organic extracts were concentrated and chromatographed (silica, benzene-EtOAc, 9:1, v/v) to give product (0.41 g, 70%, mp 94-95 °C).

Using similar methods, Creary and coworkers have prepared a number of phenylsulfonyl substituted toluene methanesulfonates for use in a solvolysis study.[92]

$$PhCBr(CH_3)SO_2Ph + AgOMs \rightarrow PhC(OMs)(CH_3)SO_2Ph + AgBr(s) \downarrow$$
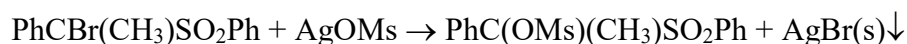
Acetonitrile was again used as the solvent, but in this case the reaction was heated to reflux for several hours. The AgBr was filtered off, and the solvent was removed in-vacuo. The products were purified by recrystallization from CH_2Cl_2.[92]

Reactions that do not employ AgOMs to introduce a mesyloxy group:

h)   *Anion Exchange of Methanesulfonate for Halide in Silanes with Cr(II):*

Chlorosilanes can be converted to mesyloxysilanes with Cr(OMs)_2 (Cr(II) compound is normally prepared and used as a DMF solvate),[23,43]

$$Cr(OMs)_2 + 2 R_3SiCl \rightarrow 2 R_3SiOMs + CrCl_2(s) \downarrow$$
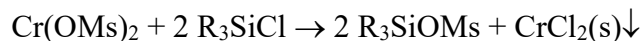
i)   *Mercuration/Demercuration of Alkenes and Alkynes with Mercuric Methanesulfonate:*

Alkenes and alkynes can be mercurated with mercuric methanesulfonate,[93 - 97]

$$RR'C=CRR' + Hg(OMs)_2 \rightarrow RR'(MsO)C-CRR'(HgOMs)$$
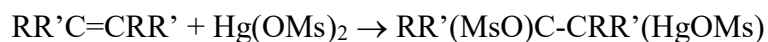
The initially formed organomercury compounds can be decomposed to mercury-free organic products with either halogen or hydride reagents,

$$RR'(MsO)C-CRR'(HgOMs) + I_2 \rightarrow RR'(MsO)C-CRR'I + HgI(OMs)$$

$$RR'(MsO)C-CRR'(HgOMs) + NaBH_4 \rightarrow RR'(MsO)C-CRR'H + Hg + NaOMs + BH_3$$
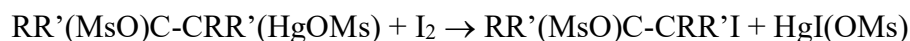
The initially formed epimercuronium ion (3 membered ring formed by the interaction of $MsOHg^+$ with the unsaturated bond) can be quenched in a two ways. The epimercuronium ion can be intercepted by mesylate to yield a β-mesyloxyalkylmercury compound, or, alternatively, the epimercuronium ion can be trapped with an *in-situ* or intramolecular nucleophile (*e.g.*, ROH) to yield the corresponding β-substituted-alkylmercury compound (*e.g.*, a β-alkoxyalkylmercury compound). The carbon mercury bond can be decomposed by halogen to yield the corresponding alkyl bromide, or, alternatively, it can be reduced with a metal hydride reagent to yield the corresponding hydrocarbon. The following procedure is illustrative:[93]

(E)-1-Ethyl-2-iodobut-1-enyl methanesulfonate: To a mixture of 3-hexyne (5 mmol) and mercuric methanesulfonate (5 mmol) was added iodine (5 mmol) in small portions at 0 °C. The reaction mixture was stirred at 0 °C till no further iodine color was observed (total reaction time of 4 h). The mercury salt was filtered off, and the organic filtrate was washed successively with 0.1 M sodium thiosulfate and saturated KI(aq). The organic phase was dried over sodium sulfate and reduced *in-vacuo*. The product was purified by chromatography on silica with hexane/ether.

j)   *α-mesyloxylation of Ketones with Thallium (III) or Cu(II) Methanesulfonate:*

Enolizable ketones can be α-mesyloxylated with $Tl(OMs)_3$,[98]

$$PhCOCH_3 + Tl(OMs)_3 \rightarrow PhCOCH_2OMs + TlOMs + MSA$$

Alkyl methyl ketones with a α-methine carbon are mesyloxylated specifically at the methine position by treatment with $Cu(OMs)_2$,[99,100]

$$CH_3COCHRR' + Cu(OMs)_2 \rightarrow CH_3COC(OMs)RR' + Cu + MSA$$

Both the Th(III) and the Cu(II) based mesyloxylations can be carried out in refluxing acetonitrile. The Cu(II) reaction can also be run neat under microwave irradiation with total reaction time decreasing from 14 hours (refluxing acetonitrile) to three minutes. Purification involves solvent extraction followed by chromatography, distillation and/or crystallization.

k)   *Activation of Thiol Esters with Mercuric Methanesulfonate:*

Thiol esters can be trans-esterified with *t*-butanol after activation with mercuric mesylate,[101]

$$RCOSR' + Hg(OMs)_2 + tBuOH \rightarrow RCOOMs \rightarrow RCOOtBu + Hg(SR')(OMs) + MSA$$

The use of mercuric ion activation of thiol esters represents one way to produce generally difficult to obtain *tert*-butyl esters. The production of β-lactones via intra-molecular esterification is also made possible via this type of thiol ester activation with mercuric methanesulfonate.[102] An intermediate carboxylic methanesulfonic acid anhydride is likely.

l)   *Solvolysis of Imides with Cupric Methanesulfonate:*

Imides can be partially methanolyzed via treatment with cupric methanesulfonate in MeOH with simultaneous generation of MSA,[103]

$$2 (RCO)(RCO)NR' + Cu(OMs)_2 + 2 MeOH \rightarrow (RCONR')_2\text{-}Cu + 2 RCOOMe + 2 MSA$$

$(RCONR')_2$-Cu + H_2S → 2 RCONHR' + CuS(s)↓
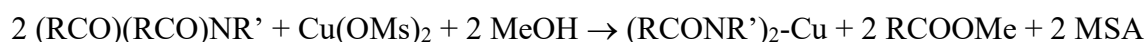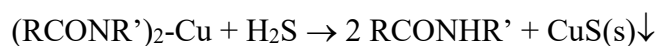
The above partial methanolysis reaction was used to convert 1,3-(bis-(3,5-dioxopiperazin-1-yl)propane to N,N'-dimethoxycarbonylmethyl-N,N'-diaminocarbonylmethyl-1,3-diaminopropane dimethanesulfonate.[29] The use of cupric methanesulfonate, as opposed to some other copper (II) salt, allowed for the direct formation of an onium methanesulfonate as the product of partial methanolysis of the *bis*-imide. The following procedure was used:[103]

N,N'-Di(methoxycarbonylmethyl)-N,N'-di(aminocarbonylmethyl)-1,3-diaminopropane dimethanesulfonate: A mixture of 1,3-*bis*(3,5-dioxopiperazin-1-yl)propane (0.1 mol), cupric methanesulfonate (0.1 mol) and dry methanol (500 ml) was stirred and heated under reflux for 48 hours. The reaction mixture was evaporated to dryness, and the residue was taken up in water (200 ml). The water solution was saturated with H_2S and then filtered. The resultant colorless solution was evaporated to dryness to yield a white solid that could be recrystallized from methanol (100 ml) containing a little water. Concentration of the crystallization mother liquors to 50 ml followed by dilution with acetone (500 ml) gave on cooling a further crop of solid providing for a total yield of 43% (mp 157-159 ºC).

m)   *Preparation of Phenyl Methanesulfonate from Peroxydimethanesulfonic Acid:*

The anodic oxidation of sodium methanesulfonate in anhydrous MSA yields a peroxide that can substitute the methanesulfonyl group for hydrogen on aromatics via an electrophilic aromatic substitution mechanism,[104]

PhH + MsOOMs → PhOMs + MSA
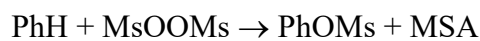
Reactions wherein a metal methanesulfonate is used as a starting material:

n)   *Preparation of MSA from a Metal Methanesulfonate:*

MSA can be prepared via the reaction of sodium methanesulfonate with HCl,[105,106,107]

NaOMs + HCl → MSA + NaCl(s)↓
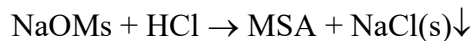
HCl is added to a concentrated solution of sodium methanesulfonate in water or methanol. The NaCl byproduct is removed by selective crystallization.

MSA can be prepared by the electrodialysis of aqueous solutions of sodium methanesulfonate,[108]

NaOMs → Na^+ (cation Ex membrane to catholyte) + OMs^- (anion Ex membrane to anolyte)

2 H_2O + 2 e^- → 2 OH^- + H_2 (catholyte, sodium hydroxide formed)

2 H_2O - 2 e^- → 2 H^+ + O_2 (anolyte, MSA formed)
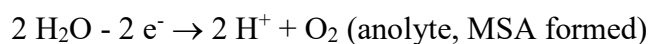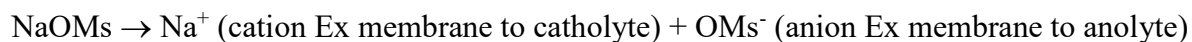
Standard salt-splitting techniques can be applied to aqueous solutions of IA or IIA metal methanesulfonates. For example, an aqueous solution of sodium methanesulfonate can be run through the central chamber of an electrodialysis cell. The methanesulfonate anion migrates into the anolyte chamber wherein it combines with an electrogenerated proton to produce MSA. The sodium cation migrates

through the cation exchange membrane into the catholyte to combine with electrogenerated hydroxide anion to yield sodium hydroxide.

MSA can be prepared from a number of metal methanesulfonates via electrowinning in an anion-exchange membrane separated electrochemical cell,[1,109]

$$M(OMs)_2 \rightarrow 2 \text{ MSA (anolyte)} + M \text{ (catholyte)}$$
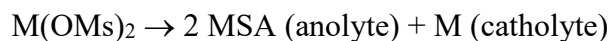
The electrode processes employed for this electrochemical technique are cathodic electrodeposition of metal and anodic generation of $H^+(aq)/O_2(g)$. The ionic current in the electrochemical cell is carried by the selective transport of methanesulfonate anions from the catholyte to the anolyte via an anion-exchange membrane. Pure MSA is generated in the anolyte, while reduced metal is generated in the cathode compartment. The metal formed in the cathode compartment is usually part of an adherent cathode deposit. Methanesulfonate salts of any metal that can be electrodeposited from aqueous solution can theoretically be used as a starting materials for this electrochemical reaction. The technique was designed for the recovery of MSA value from Fe(II), Fe(III) and Ni(II) salts of MSA.

o)   *Sodium Methanesulfonate as a Raw Material for Producing Sulfonyl Halides:*

Sodium methanesulfonate can be reacted with PCl_5 to yield methanesulfonyl chloride,[110]

$$CH_3SO_2ONa + PCl_5 \rightarrow CH_3SO_2Cl + POCl_3 + NaCl$$

A mixture of sodium methanesulfonate and sodium methylsulfate, produced via the reaction of sodium sulfite with dimethylsulfate, was reacted with PCl_5 to yield a product containing methanesulfonyl chloride (MSC). The MSC was purified by distillation from the crude product mixture.

Sodium methanesulfonate can be converted into an N,N-dialkylmethanesulfonamide via intermediate conversion to methanesulfonyl bromide through treatment with $Ph_3P\text{-}Br_2$,[111]

$$CH_3SO_2ONa + Ph_3P\text{-}Br_2 \rightarrow CH_3SO_2Br + Ph_3PO + NaBr$$
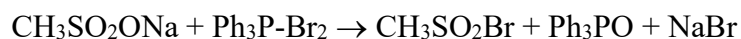
The methanesulfonyl bromide formed was reacted with a secondary amine in the presence of triethylamine to yield an N,N-dialkylmethanesulfonamide.

p)   *Metal Methanesulfonates as Simple Substrates for Ion-Exchange:*

Silver methanesulfonate can be used as a raw material for the production of complex silver salts,[112]

$$AgOMs + PPh_3 + KTm \rightarrow AgTm\text{-}PPh_3 + KOMs \quad (KTm = \text{potassium salt of a complex borate})$$

A mixture of KTm (0.39 g, 1 mmol) and triphenylphosphine (0.26 g, 1 mmol) in THF (30 ml) was added to AgOMs (0.26 g, 1 mmol) in THF (20 ml) at RT. After the addition, the solution was stirred overnight. The volatile materials were removed under reduced pressure, and the residue was extracted into chloroform. The suspension was filtered, and the solvent was removed. Diethyl ether was then added, and the colorless precipitate obtained was filtered off, washed and shown to be AgTm(PPh$_3$) (70% yield). In this reaction, silver methanesulfonate serves as a simple raw material for an ion exchange.

Sodium methanesulfonate can be used to prepare ammonium methanesulfonate,[113]

$$2 \text{ NaOMs} + (\text{NH}_4)_2\text{SO}_4 \rightarrow 2 \text{ NH}_4\text{OMs} + \text{K}_2\text{SO}_4$$
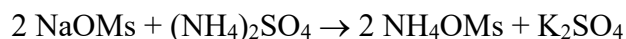
Solvents having polarity parameter E_t = 35-60 Kcal/mol (25 °C) favor the forward reaction. Typical reaction conditions involve heating to 40 °C for 5 hours in a MeOH solvent.

Sodium methanesulfonate can be used to regenerate anion-exchange resins that are in turn used to convert complex pyridinium chlorides to the corresponding pyridinium methanesulfonates,[114]

$$\text{Py}^+\text{Cl}^- + \text{OMs}^- \text{ form of anion-exchange resin} \rightarrow \text{Py}^+\text{OMs}^- + \text{Cl}^- \text{ form of anion-exchange resin}$$
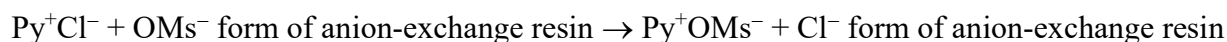
The pyridinium methanesulfonate produced was tested as an aqueous soluble antidote for organophosphorous nerve gas poisoning.

q)   *Lanthanide Methanesulfonates as Starting Materials for Ln(Cp)₃ compounds:*

Tricyclopentadienyl lanthanide complexes can be prepared from anhydrous lanthanide (III) methanesulfonates,[115]

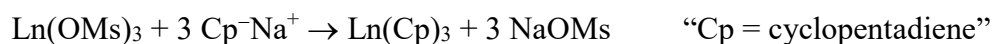$$\text{Ln(OMs)}_3 + 3 \text{ Cp}^-\text{Na}^+ \rightarrow \text{Ln(Cp)}_3 + 3 \text{ NaOMs} \qquad \text{"Cp = cyclopentadiene"}$$

The general reaction was carried out by reacting sodium cyclopentadienide (60 mmol) with anhydrous Ln(OMs)_3 (Ln = Nd, Yb) (15 mmol) in anhydrous THF under reflux for 6 h. The resulting solution was filtered free of byproduct sodium methanesulfonate and then concentrated *in-vacuo* to a solid. The crude solid product was purified by vacuum sublimation. Anhydrous lanthanum (III) methanesulfonates were used in preference to alternative starting materials (*e.g.*, LnCl_3) because they could be handled more conveniently. In particular, the anhydrous lanthanum (III) methanesulfonates were found to be much less hygroscopic than the corresponding lanthanum (III) chlorides.

r)   *Silver Sulfide Complexes from Silver Methanesulfonate:*

Complexes of silver salts with dialkyl sulfides (2 dialkyl sulfides per Ag) can be formed with silver methanesulfonate serving as the starting material,[116]

$$\text{AgOMs} + 2 \text{ R}_2\text{S} \rightarrow (\text{R}_2\text{S})_2\text{AgOMs}$$
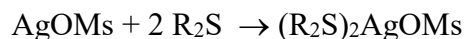
The reaction can be carried out at RT in methylene chloride, and the product can be precipitated by the addition of ether to the reaction solvent. The final product is typically collected by vacuum filtration and dried to constant weight *in-vacuo*.

Finally, we will review reactions wherein a metal methanesulfonate is used in preference to alternative salts because of its uniquely high solubility. It should be noted that the uniquely high aqueous solubility of a number of metal methanesulfonate salts (see Table 1 in this paper) has enabled the development of some very important electroplating and metal finishing applications (*e.g.*, Sn/Pb electroplating).[1] In the area of stoichiometric synthesis, there is only one important application of this type, the use of Ce(III)/Ce(IV) methanesulfonates in the metal couple mediated electrochemical oxidation of aromatic substrates.

Reactions wherein metal methanesulfonate has high solubility in reaction solvent:

s)   *Indirect Electrochemical Oxidation of Aromatics with Ce(IV) Methanesulfonate:*

A number of indirect electrochemical oxidations of aromatic substrates to quinones and/or benzaldehyde type compounds have been carried out with Ce(III)/Ce(IV) methanesulfonate.[117]   The commercial application of this reaction is sometimes referred to as the "Grace Process" owing to its initial development at W. R. Grace Corporation's Washington Research Center.

The oxidation of toluene to benzaldehyde is exemplary:

$$PhCH_3 + 4\ Ce(OMs)_4 + H_2O \rightarrow PhCHO + 4\ Ce(OMs)_3 + 4\ MSA$$
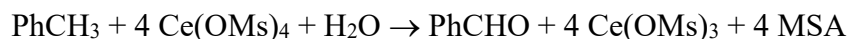
The process involves the anodic oxidation of Ce(III) to Ce(IV) at an inert anode in an aqueous MSA solution. The aqueous MSA solution of Ce(IV) is next vigorously mixed with an organic substrate, either neat or in an organic solvent, in order to carry out the oxidation. Following completion of the oxidation, the mixing is stopped and the aqueous and organic phases are allowed to separate. The aqueous solution of spent Ce(III) methanesulfonate is transported back to a separate electrochemical cell for reoxidation to Ce(IV) methanesulfonate, while the reacted organic phase is taken off for final purification. The preparation of quinone and benzaldehyde derivatives from appropriate aromatic substrates has been found to be one of the most ideal applications of this method. The method was enabled by the use of ceric methanesulfonate, as opposed to some alternative cerium (IV) salt, because of the stability of the methanesulfonate anion to the oxidizing conditions employed and because of the unusually high aqueous and organic solubility of ceric methanesulfonate. The high aqueous solubility of ceric methanesulfonate enables the electrochemical oxidation of Ce(III) to Ce(IV) in the first place, while the high organic solubility of Ce(IV) methanesulfonate enhances the transport of Ce(IV) into the organic phase during the main oxidation. Further information can be found in the extensive literature that has been published concerning this process.[117]

Some Further Work:

As this paper was being approved for publication, some additional interesting reactions of metal methanesulfonates have been published. Cuccovia *et al.* found that sodium methanesulfonate is useful for the conversion of arenediazonium salts to phenols via an intermediate phenyl methanesulfonate.[118] A group at Liaoning University of Petroleum and Chemical Technology in Fushun, China found that a number of transition metal and lanthanide metal methanesulfonate salts are useful as reusable esterification catalysts.[119] A soluble onium salt form of paclitaxel has been prepared from the corresponding tosylate by reaction with sodium methanesulfonate, and camostat methanesulfonate has been prepared by the reaction of camostat chloride with alkali metal methanesulfonate salts.[120,121]

Some interesting work concerning the preparation of metal methanesulfonate salts has also recently been published. A group at Ebara Udylite Company in Japan has examined the preparation of lead (II) methanesulfonate from mixed Pb(IV)/Pb(II) oxides in the presence of phenols, and a group at Eindhoven University of Technology has conducted a thorough study of the electrochemical dissolution of tin into aqueous methanesulfonic acid solution.[122,123] Also, the preparation of lanthanum (III) methanesulfonate via reaction of lanthanum oxide and MSA has been described.[124] The preparation of a number of simple aqueous soluble complexes of silver methanesulfonate have recently been described.[125] A patent outlining the preparation of methanesulfonic acid from metal methanesulfonate salts has been published.[126]

The following metal methanesulfonate salts have been registered more recently than those previously discussed:

Alkali & Alkaline Earth Metal Methanesulfonates				
Cation	Hydrate	Solvate	CAS #	Bibliographic References
Ca^{+2}	x	-	212133-92-1	127

Transition Metal Methanesulfonates				
Cation	Hydrate	Solvate	CAS #	Bibliographic References
Mn^{+3}	-	-	200123-62-2	128
Co^{+3}	-	-	610280-31-4	128
Zn^{+2}	3	-	586390-53-6	119
Au^{+1}	-	-	176206-14-7	129

Lanthanide Methanesulfonates				
Cation	Hydrate	Solvate	CAS #	Bibliographic References
La^{+3}	4	-	586390-54-7	119
Nd^{+3}	2	-	362520-80-7	119, 130
Sm^{+3}	2	-	190911-02-5	67, 130
Eu^{+3}	2	-	362520-85-2	130
Gd^{+3}	2	-	362520-86-3	130
Tb^{+3}	2	-	190911-03-6	67, 130
Dy^{+3}	2	-	362520-87-4	130
Ho^{+3}	2	-	362520-88-5	130
Er^{+3}	2	-	362520-81-8	130
Tm^{+3}	2	-	362520-90-9	130
Yb^{+3}	2	-	362520-91-0	130
Lu^{+3}	2	-	362520-93-2	130

Mixed Metal Methanesulfonates				
Cation	Hydrate	Solvate	CAS #	Bibliographic References
Fe^{+x}, Sn^{+x}	-	-	220259-07-4	126

Calcium methanesulfonate was studied as a potential additive for cement.[127] The gold salt (AuOMs) of methanesulfonic acid has been prepared for use in an electroplating solution.[129] The lanthanide dihydrates were all prepared by reaction of the corresponding metal oxides with methanesulfonic acid (reference describes the structure and thermal properties of hydrated lanthanide methanesulfonates).[130]

Summary:

Metal methanesulfonates can be prepared in a number of ways. The utility of metal methanesulfonates as components of electroplating solutions or as catalysts greatly exceeds their utility in all other areas. Still, the stoichiometric synthetic applications of metal methanesulfonate salts are significant, and preparative chemists will profit by staying current with all the published applications of these interesting compounds.

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