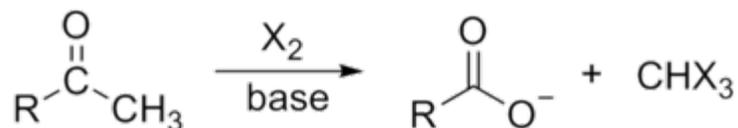


# Haloform reaction

From Wikipedia, the free encyclopedia

The **haloform reaction** is a chemical reaction where a haloform (CHX<sub>3</sub>, where X is a [halogen](#)) is produced by the exhaustive [halogenation](#) of a methyl [ketone](#) (a molecule containing the R–CO–CH<sub>3</sub> group) in the presence of a [base](#).<sup>[1]</sup> R may be [alkyl](#) or [aryl](#). The reaction can be used to produce [chloroform](#) (CHCl<sub>3</sub>), [bromoform](#) (CHBr<sub>3</sub>), or [iodoform](#) (CHI<sub>3</sub>).



R = H, alkyl, aryl

X = Cl, Br, I

## Contents [hide]

- 1 Scope
- 2 Mechanism
- 3 Uses
- 4 Iodoform test
- 5 History
- 6 Net reaction
- 7 Byproducts
- 8 References

## Scope [edit]

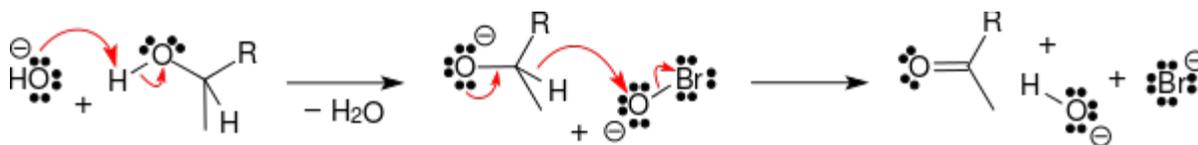
Substrates that successfully undergo the haloform reaction are methyl ketones and secondary [alcohols](#) oxidizable to methyl ketones, such as [isopropanol](#). The only primary alcohol and [aldehyde](#) to undergo this reaction are [ethanol](#) and [ethanal](#), respectively. 1,3-Diketones such as [acetylacetone](#) also give the haloform reaction. β-ketoacids such as [acetoacetic acid](#) will also give the test upon heating. Acetyl chloride and acetamide don't give this test. The halogen used may be [chlorine](#), [bromine](#), [iodine](#) or [sodium hypochlorite](#).<sup>[2]</sup> [Fluoroform](#) (CHF<sub>3</sub>) cannot be prepared from a methyl ketone by the haloform reaction due to the instability of [hypofluorite](#),<sup>[clarification needed]</sup> but compounds of the type RCOCF<sub>3</sub> do cleave with base to produce fluoroform; this is equivalent to the second and third steps in the process shown above.

## Mechanism [edit]

In the first step, the halogen disproportionates in the presence of [hydroxide](#) to give the halide and hypohalite (example with bromine, but reaction is the same in case of chlorine and iodine; one should only substitute Br for Cl or I):

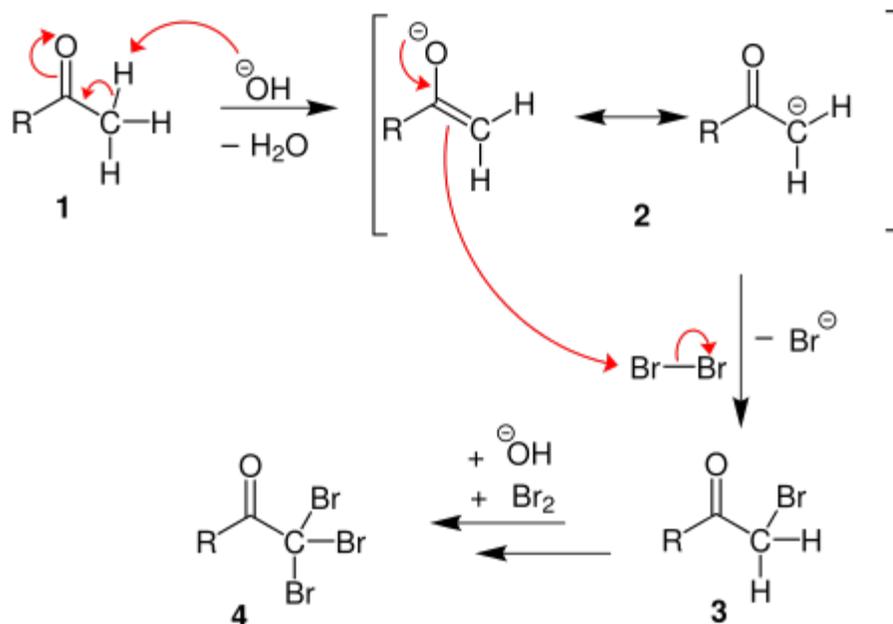


If a secondary alcohol is present, it is oxidized to a ketone by the hypohalite:

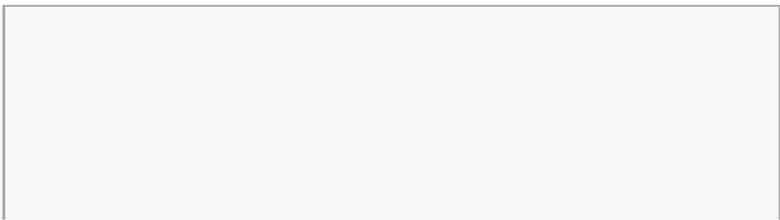
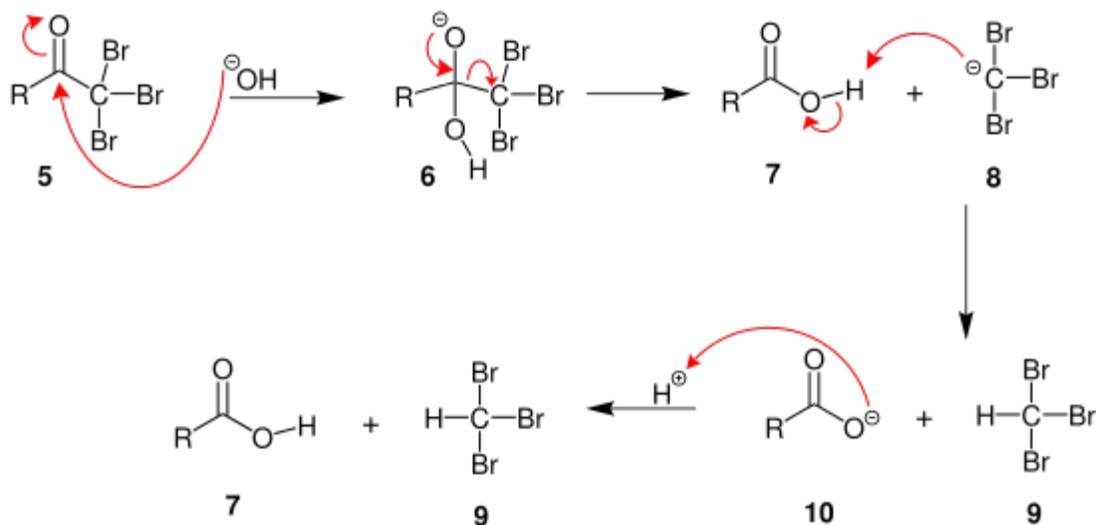


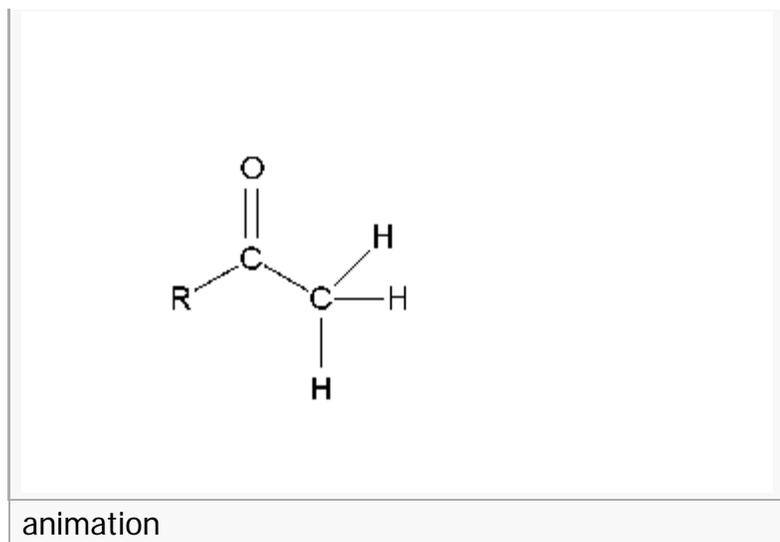
If a methyl ketone is present, it reacts with the hypohalite in a three-step process:

(1) Under basic conditions, the ketone undergoes [keto-enol tautomerization](#). The enolate undergoes electrophilic attack by the hypohalite (containing a halogen with a formal +1 charge).



(2) When the  $\alpha$  position has been exhaustively halogenated, the molecule undergoes a [nucleophilic acyl substitution](#) by hydroxide, with  $^-CX_3$  being the [leaving group](#) stabilized by three [electron-withdrawing groups](#). In the third step the  $^-CX_3$  anion abstracts a proton from either the solvent or the carboxylic acid formed in the previous step, and forms the haloform. At least in some cases ([chloral hydrate](#)) the reaction may stop and the intermediate product isolated if conditions are acidic and hypohalite is used.





## Uses [edit]

This reaction was traditionally used as a [chemical test](#) for [qualitative organic analysis](#) to determine the presence of a methyl ketone, or a secondary alcohol oxidizable to a methyl ketone through the [iodoform test](#). Nowadays, spectroscopic techniques such as [NMR](#) and [infrared](#) are easy and quick to perform instead of qualitative tests. Iodoform reaction is used as test reaction of ethyl alcohol in given sample of alcohols.

It was formerly used to produce iodoform, bromoform, and even chloroform industrially.<sup>[*[citation needed](#)*]</sup>

In [organic chemistry](#), this reaction may be used to convert a terminal methyl ketone into the analogous carboxylic acid.

## Iodoform test [edit]

When iodine and sodium hydroxide are used as the reagents, a positive reaction gives iodoform. [Iodoform](#) (CHI<sub>3</sub>) is a pale-yellow substance. Due to its high [molar mass](#) caused by the three [iodine](#) atoms, it is solid at room temperature (cf. chloroform and bromoform). It is [insoluble](#) in water and has an [antiseptic](#) smell. A visible precipitate of this compound will form from a sample only when either a methyl ketone, ethanal, ethanol, or a methyl secondary alcohol is present.



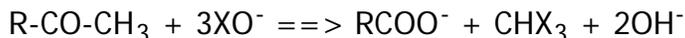
Negative and positive iodoform test

## History [edit]

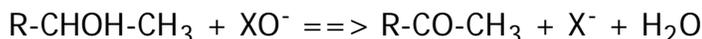
The haloform reaction is one of the oldest [organic reactions](#) known.<sup>[3]</sup> In 1822, [Georges-Simon Serullas](#) added potassium metal to a solution of [iodine](#) in [ethanol](#) and water to form potassium formate and iodoform, called in the language of that time ***hydroiodide of carbon***.<sup>[4]</sup> In 1831, [Justus von Liebig](#) reported the reaction of [chloral](#) with [calcium hydroxide](#) to form chloroform and calcium formate. The reaction was rediscovered by [Adolf Lieben](#) in 1870. The iodoform test is also called the **Lieben haloform reaction**. A review of the Haloform reaction with a history section was published in 1934.<sup>[5]</sup>

## Net reaction [edit]

The net reaction starting from a methyl ketone and hypohalite may be written:



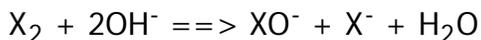
The oxidation of alcohol to a ketone may be written:



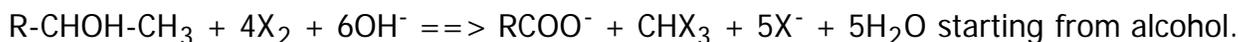
The net reaction starting from alcohol and hypohalite is therefore:



Note that using hypohalite the alkalinity will not only be maintained but enhanced even though one hydroxide ion is consumed in the final reaction step. Using dihalogen hydroxide ions will instead be consumed in the halogen disproportionation step:



Starting from dihalogen the net reactions will be:



## Byproducts [edit]

The ketone carbon chain will lose its methyl group forming a carboxylate group at the carbonyl position. In the alkaline environment it is expected to be present in ion form. If the ketone is [acetone](#) the [carboxylate](#) byproduct ( $\text{RCOO}^-$ ) would be an [acetate](#) ion. Depending on conditions water, hydroxide and halide ions will also form, see net reaction formulas. Note that halide ions form in the dihalogen disproportionation and alcohol oxidation steps, not the haloform reaction per se as is the case for water.

## References [edit]

- ↑ Chakrabartty, in Trahanovsky, ***Oxidation in Organic Chemistry***, pp 343–370, Academic Press, New York, **1978**
- ↑ ***Chemical Synthesis Accelerated by Paper Spray: The Haloform Reaction*** Ryan M. Bain, Christopher J. Pulliam, Shannon A. Raab, and R. Graham Cooks *Journal of Chemical Education* 2016 93 (2), 340-344  
doi:10.1021/acs.jchemed.5b00263
- ↑ László Kürti and Barbara Czako (2005). ***Strategic Applications of Named Reactions in Organic Synthesis***. Amsterdam: Elsevier. ISBN 0-12-429785-4.
- ↑ Georges-Simon Surellas, ***Notes sur l'Hydriodate de potasse et l'Acide hydriodique. – Hydriodure de carbone; moyen d'obtenir, à l'instant, ce composé triple***  [Notes on the hydroiodide of potassium and on hydroiodic acid – hydroiodide of carbon; means of obtaining instantly this compound of three elements] (Metz, France: Antoine, 1822). On pages 17–20, Surellas produced iodoform by passing a mixture of iodine vapor and steam over red-hot coals. However, later, on pages 28–29, he produced iodoform by adding potassium metal to a solution of iodine in ethanol (which also contained some water).
- ↑ Reynold C. Fuson and Benton A. Bull (1934). "The Haloform Reaction". ***Chemical Reviews*** **15** (3): 275–309. doi:10.1021/cr60052a001 .

Categories: [Chemical tests](#) | [Organic redox reactions](#) | [Carbon-heteroatom bond forming reactions](#)