

Adducts of Mesitaldehyde and Strong Molecular Acids

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Mesitaldehyde has been found to form two series of crystalline adducts with strong mineral acids. In one series, the molar ratio of mesitaldehyde to molecular acid is 1:1, the stability order being $\text{BF}_3 > \text{HClO}_4 > \text{HI} > \text{HBr} > \text{HCl}$. In the other series, the molar ratio of aldehyde to acid is 2:1 and the stability order is $\text{HClO}_4 > \text{HI} > \text{HBr}$. The 1:1 adducts are probably oxonium salts. The structure of the very hygroscopic but otherwise stable 2:1 mesitaldehyde-perchloric acid adduct was not revealed by a detailed study of its spectral and chemical properties. All chemical treatments of it yielded mesitaldehyde or a compound obtainable directly from mesitaldehyde.

Solid 2:1 adducts of mesitaldehyde with perchloric acid, hydrogen iodide, and hydrogen bromide have been prepared. Under slightly different conditions solid 1:1 adducts of mesitaldehyde with perchloric acid, hydrogen iodide, hydrogen bromide, hydrogen chloride, and boron trifluoride are produced.

Only the 1:1 mesitaldehyde-boron trifluoride and 2:1 mesitaldehyde-perchloric acid adducts were stable when stored under anhydrous conditions. The properties of the latter compound were investigated in some detail. However, the complete elucidation of its structure could be achieved only by X-ray crystallographic analysis, as described in the accompanying paper.¹

Attempts to cross-condense mesitaldehyde with anisole or mesitylene (as solvents) in the presence of 70% perchloric acid led only to the mesitaldehyde-perchloric acid 2:1 adduct. Some attempts were made to extend the reaction of 2:1 adduct formation to other carbonyl compounds. Preliminary experiments indicate that both pentamethylbenzaldehyde and 2,4,6-trimethoxybenzaldehyde give the same sort of adducts as does mesitaldehyde. Acetomesitylene failed to yield any adducts.

1:1 Adducts. The most stable and well-defined 1:1 adduct was that with boron trifluoride. It was prepared by the addition of boron trifluoride to a solution of mesitaldehyde in anhydrous methylene chloride. Its composition was inferred from its elemental analysis and the intensity of its ultraviolet spectrum in ethanol, in which complete dissociation to mesitaldehyde occurs.

The 1:1 adducts with hydrogen bromide or perchloric acid precipitated in well-defined crystalline form on the addition of hydrogen bromide or perchloric acid to a solution of mesitaldehyde in acetic acid. The hydrogen chloride adduct precipitated upon removal of the

solvent from an ether solution of mesitaldehyde and excess hydrogen chloride. The hydrogen iodide 1:1 adduct formed on attempted recrystallization of the 2:1 adduct from benzene (this is opposite to the result for the perchloric acid adducts, in which case the 2:1 adduct precipitated on attempted recrystallization of the 1:1 adduct from benzene). Attempts to purify the latter adducts by sublimation or recrystallization proved fruitless. Furthermore, they were quite unstable, and all except the hydrogen iodide were very hygroscopic. Consequently, no elemental analyses were made except for an iodine analysis on the hydrogen iodide adduct. However, neutral equivalents were obtained on crude, freshly prepared crystals and these are in rough agreement with the assigned molar ratio as seen in Table I. It is to be noted that the colors, crystalline forms, melting points, and solubilities of the 1:1 adducts differ from those of the corresponding 2:1 adducts.

Table I. Properties of Mesitaldehyde Adducts^a

Acid	Color	M.p., °C.	Neut. equiv.	
			Obsd.	Calcd.
1:1 Adducts				
HClO_4	Light yellow	95–100 dec.	290	249
HI	Yellow ^b	125–130 dec.	294 ^c	275
HBr	Colorless	80–85 dec.	257	229
HCl	Colorless	45–47 dec.	191	185
BF_3	Colorless	171–172	(221) ^d	216
2:1 Adducts				
HClO_4	Deep yellow	148–149 dec.	398	397
HI	Deep orange	70–80	446	423
HBr	Deep yellow	40–50	388	377
HCl	Light yellow	8–12	...	333

^a All adducts are crude except 1:1 mesitaldehyde- BF_3 and 2:1 mesitaldehyde- HClO_4 . ^b Becomes coated brown on exposure to air. ^c Anal. Calcd. for $\text{C}_{10}\text{H}_{13}\text{IO}$: I, 46.2. Found: I, 48.1. ^d Equivalent weight obtained by ultraviolet spectrophotometric method.

The stability order of the 1:1 adducts appears to be $\text{BF}_3 > \text{HClO}_4 > \text{HI} > \text{HBr} > \text{HCl}$. Although very hygroscopic, the boron trifluoride adduct was easily purified by sublimation and could be kept indefinitely in a sealed vial. The perchloric acid adduct suffered slight discoloration on being stored in a desiccator for several weeks. The hydrogen halide adducts lost hydrogen halide on standing, the hydrogen chloride decomposing within a few hours to leave a residue of pure mesitaldehyde.

The securing of good spectral data of the adducts was complicated by their hygroscopic behavior and instability. Also, rather extensive dissociation to mesitaldehyde occurred in solvents in which ultraviolet

(1) C. D. Fisher, L. H. Jensen, and W. M. Schubert, *J. Am. Chem. Soc.*, **87**, 33 (1965).

spectra could be obtained. For example, the ultraviolet spectrum of the 1:1 perchloric acid adduct in carefully dried acetonitrile had bands of approximately equal intensity at 265 and 310 $m\mu$. The lower wave-length band probably corresponds to that of free mesitaldehyde, the intense principal band of which is centered at 265 $m\mu$ in acetonitrile. The 310- $m\mu$ band probably is that of the oxygen conjugate acid of mesitaldehyde, which absorbs at 315 $m\mu$ in strong sulfuric acid.²

The ultraviolet spectrum of the boron trifluoride adduct in dry methylene chloride showed bands at 265 and 304 $m\mu$ with relative ϵ -values of 2:1. Upon the dropwise addition of ethanol, the 265- $m\mu$ band grew at the expense of the 304- $m\mu$ band. About 5 drops of ethanol added to the Cary cell was sufficient to cause complete disappearance of the 304- $m\mu$ band, and the final spectrum corresponded to that of pure mesitaldehyde. The results would indicate that the 304- $m\mu$ band is that of undissociated boron trifluoride-mesitaldehyde adduct.

The infrared spectrum of the 1:1 perchloric acid adduct in a dry potassium bromide pellet resembled that of mesitaldehyde in the carbonyl region, except that the C=O stretching frequency was lowered to 1660 cm^{-1} from the value of 1688 cm^{-1} for mesitaldehyde. No distinct OH band was observed. The boron trifluoride adduct in methylene chloride showed sharp bands at 1642 (strong) and 1680 cm^{-1} (medium). It is possible that the latter band is caused by some dissociated mesitaldehyde.

All the evidence gathered indicates that the 1:1 adducts are oxygen conjugate acids of mesitaldehyde. Similar adducts of other aldehydes have previously been encountered. Kirby and Reid assigned an oxygen-protonated structure to yellow salts obtained from perchloric acid and 1-formylazulene, 1,3-diformylazulene, and 1-formylguaiazulene. The adduct of 1-formylguaiazulene was quite stable, whereas the other two salts readily reverted to the parent aldehydes upon exposure to air.³ An oxygen-protonated structure also has been assigned by Hafner and Bernhard to the salt formed between 4,6,8-trimethyl-1-formylazulene and perchloric acid. A 1:1 hydrogen chloride adduct also was reported.⁴ In agreement with these structural assignments is the conclusion of Long and Schulze based on nuclear magnetic resonance studies that 1-formylazulene is oxygen-protonated in trifluoroacetic acid solution.⁵

Rubalcava and Thompson reported that formylferrocene forms a hydrochloride salt under pressure and concluded that the formyl oxygen is protonated.⁶ A 1:1 boron trifluoride-acetone adduct has been reported by Chalandon and Susz.⁷

2:1 Adducts. The 2:1 mesitaldehyde-hydrogen halide adducts were prepared by passing the dry hydrogen halide gas into the aldehyde in the absence of solvent. With hydrogen iodide and hydrogen bromide, well-defined crystals formed rapidly. Partial puri-

fication was achieved by trituration or thorough washing with dry hexane. The hydrogen chloride adduct appeared to melt below room temperature and was not isolated. All of the hydrogen halide adducts were highly hygroscopic. When kept dry they evolved hydrogen halide gas, the stability order being $HI > HBr > HCl$.

Attempts to purify the hydrogen halide 2:1 adducts were unsuccessful. The hydrogen bromide adduct was too unstable and the hydrogen iodide adduct, on recrystallization from dry benzene, was converted to the 1:1 adduct. Neutralization equivalents perforce had to be determined on freshly prepared crude samples and agree approximately with the assigned 2:1 molar ratio (Table I).

The perchloric acid 2:1 adduct was originally prepared by attempted recrystallization of the 1:1 adduct from benzene. It could be prepared directly by the addition of 70% perchloric acid to a strong solution of mesitaldehyde in acetic acid (the use of too large an excess of perchloric acid favored formation of the 1:1 adduct). No crystal formation took place when the perchloric acid was less than 56% in strength. The 2:1 adduct sublimed readily, in contrast to the behavior of the 1:1 adduct, and sublimation proved to be the best method of purification.

The adduct could be kept indefinitely when stored in a desiccator, but in the air it absorbed moisture rapidly, decomposing into mesitaldehyde. Carbon, hydrogen, and chlorine analyses and the neutralization equivalent all are in excellent agreement with the assigned ratio of two mesitaldehyde units to one molecular perchloric acid unit.

The infrared spectrum of the 2:1 perchloric acid adduct in Nujol or Kel F mull was markedly different from that of mesitaldehyde. The sharp carbonyl band found at 1690 cm^{-1} for liquid mesitaldehyde was replaced by a less intense jagged broad area of absorption between 1680 and 1800 cm^{-1} . No distinct O-H stretching absorption was observed unless a weak, broad, ill-defined absorption between 1800 and 2000 cm^{-1} can be ascribed to a hydrogen bonded O-H. The background absorption was unusually strong between 750 and 1600 cm^{-1} , but bands characteristic of the perchlorate ion were clearly located at 1114 and 1093 cm^{-1} .⁸

When irradiated with ultraviolet light, the solid adduct displayed a bright yellow-green fluorescence. By contrast, the solid 1:1 adduct fluoresced only slightly, perhaps owing to the presence of some of the 2:1 adduct as an impurity. The obtaining of an ultraviolet spectrum of the 2:1 adduct was complicated by the fact that it has very limited solubility in nonpolar solvents. Sufficient adduct could be dissolved in carefully dried acetonitrile for a spectrum to be obtained. Overlapping but distinct spectral bands were found at 265, 310, and 340 $m\mu$ of relative intensity 14:7:5.3. The addition of 0.1 ml. of ethanol to the Cary cell caused the complete disappearance of the 340- $m\mu$ band, decreased the intensity of the 310- $m\mu$ band, and increased the intensity of the 265- $m\mu$ band. The addition of 0.3 ml. more of ethanol caused the complete disappearance of the band at 310 $m\mu$. The spectrum now corresponded to that

(2) W. M. Schubert and H. Burkett, *J. Am. Chem. Soc.*, **78**, 65 (1956).

(3) E. C. Kirby and D. H. Reid, *J. Chem. Soc.*, 494 (1960).

(4) K. Hafner and C. Bernhard, *Ann.*, **625**, 108 (1959).

(5) F. A. Long and J. Schulze, *Proc. Chem. Soc.*, 364 (1962).

(6) H. E. Rubalcava and J. B. Thompson, *Spectrochim. Acta*, **18**, 449 (1962).

(7) P. Chalandon and B. P. Susz, *Helv. Chim. Acta*, **41**, 697 (1958).

(8) S. D. Ross, *Spectrochim. Acta*, **18**, 225 (1962).

of pure mesitaldehyde in acetonitrile. The 340- μ band may correspond to undissociated 2:1 adduct, whereas the 310- μ band probably corresponds to 1:1 adduct.

Chemical Properties of the Mesitaldehyde-Perchloric Acid 2:1 Adduct. All reactions attempted on the 2:1 adduct led either to the production of mesitaldehyde or a derivative obtainable directly from mesitaldehyde. In hydroxylic solvents the adduct immediately dissociated into mesitaldehyde and perchloric acid. Pyrolysis of the adduct yielded mesitylene in 40% yield, presumably as the result of acid-catalyzed decarbonylation of mesitaldehyde.² Reduction, either catalytically or with lithium aluminum hydride, led to the same products obtained by reduction of mesitaldehyde. Attempts to transfer hydride ion to the adduct by treatment with cycloheptatriene or triphenylmethane⁹ were unsuccessful. Acetylation of either the 2:1 or 1:1 adduct gave 2,4,6-trimethylcinnamic acid in good yield. Attempted oxidation with manganese dioxide in dioxane led to the isolation of mesitaldehyde alone. Finally, the adduct prepared from deuterio-mesitaldehyde (MesCDO) was decomposed in water and yielded deuterio-mesitaldehyde back again; *i.e.*, no exchange of the aldehydic deuterium had occurred.

It was not possible from the spectral and chemical evidence to reach any definite conclusion about the structure of the 2:1 adducts. The ease of their reversion back to mesitaldehyde seemed to indicate some sort of molecular complex. A crystallographic investigation of the 2:1 mesitaldehyde-perchloric acid reveals it to be indeed an interesting molecular complex.¹

Experimental

The preparation of mesitaldehyde-strong acid adducts containing no spurious colored impurities required that the mesitaldehyde used be in highly pure form. Commercial mesitylene (Eastman) was purified *via* the sulfonic acid.¹⁰ Mesitylene was converted to mesitaldehyde by means of the Gattermann reaction¹¹ and the aldehyde purified by careful fractional distillation.

Because of the hygroscopic nature of the crystalline adducts, filtrations were carried out either in a drybox or with the aid of a special funnel fitted with a drying tube. Adducts were stored over phosphorus pentoxide and sodium hydroxide in a vacuum desiccator. Transformations of the adducts were carried out in a drybox.

Mesitaldehyde-Perchloric Acid 1:1 Adduct. To a solution of 5.0 g. of mesitaldehyde in 20 ml. of cold benzene was added dropwise 4.0 ml. of 70% perchloric acid. The yellow crystals (9.3 g.) were recovered by suction filtration and washed several times with dry benzene. Drying over phosphorus pentoxide and sodium hydroxide for 20 hr. in a vacuum desiccator gave 8.9 g. of pale yellow crystals, m.p. 110–115° dec.

(9) H. J. Dauben, Jr., and L. M. McDonough, Abstracts, 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 9–14, 1962, p. 55Q; L. M. McDonough, Ph.D. Thesis, University of Washington, 1959.

(10) L. I. Smith and O. W. Cass, *J. Am. Chem. Soc.*, **54**, 1603 (1932).

(11) R. C. Fuson, E. C. Horning, S. P. Rowland, and M. L. Ward, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 549.

Mesitaldehyde-Hydrogen Iodide 1:1 Adduct. Hydrogen iodide gas was bubbled into a cold solution of 4.0 g. of mesitaldehyde in 10 ml. of dry benzene to yield 1.0 g. of a red crystalline material. Passing more hydrogen iodide into the filtrate gave a second crop of red crystals (2.5 g.). Repeating the process gave an additional 1.5 g. of orange-yellow crystals. The combined crystalline product, which had been washed with benzene, then hexane, was placed over phosphorus pentoxide and sodium hydroxide in a desiccator. The crystals became dark and oily. Recrystallization from benzene gave brownish orange flakes, m.p. 120–125° dec. Sublimation under 5 mm. pressure giving a brownish-purple sublimate, m.p. 128–131° dec. The brown-purple color is believed to be due to a coating of free iodine since suspending the crystals in carbon tetrachloride produced a violet solution. The suspended crystals were yellow-orange in color but quickly acquired a brownish coat upon exposure to air. The crystals were not hygroscopic. However, they slowly evolved hydrogen iodide.

The infrared spectrum showed a strong band at 330 cm^{-1} but none near 1690 cm^{-1} in a potassium bromide pellet. In carbon tetrachloride solution, ultraviolet maxima at 267 and 296 μ were observed.

Mesitaldehyde-Hydrogen Bromide 1:1 Adduct. Dry hydrogen bromide was passed into a solution of 1.0 g. of mesitaldehyde in 3 ml. of glacial acetic acid. A yellow precipitate formed immediately. It was collected by suction filtration and washed with hexane; m.p. 80–85°. In a desiccator over phosphorus pentoxide, the crystals rapidly evolved hydrogen bromide and became oily. They could be stored in a stoppered vial for a few days.

Mesitaldehyde-Hydrogen Chloride 1:1 Adduct. Dry hydrogen chloride was passed into a solution of 1.0 g. of mesitaldehyde in 5 ml. of dry ether, yielding a light yellow solution. The solution was allowed to stand for 5 days and then the ether was allowed to evaporate. A residue of white hygroscopic needles remained, m.p. 45–47° dec. These could be washed with hexane but fumed easily in moist air and rapidly became oily in a desiccator.

Mesitaldehyde-Boron Trifluoride 1:1 Adduct. A solution of 2.0 g. of mesitaldehyde in 25 ml. of dry methylene chloride was saturated with boron trifluoride. The solution was concentrated and the resulting precipitate was collected by suction filtration and washed with methylene chloride. Sublimation yielded 0.8 g. of white needles, m.p. 171–172°. In dry methylene chloride the ultraviolet spectrum had bands at 265 (mesitaldehyde) and 305 μ (adduct), intensity ratio 2:1. In ethanol, the ultraviolet spectrum corresponded exactly to that of mesitaldehyde. The observed concentration of mesitaldehyde was $6.30 \times 10^{-5} M$ as compared to a calculated value of $6.15 \times 10^{-5} M$ based on an assumed 1:1 complex. The infrared spectrum in methylene chloride showed strong bands at 1642 and 1680 cm^{-1} (the carbonyl band of mesitaldehyde is at 1690 cm^{-1}). This compares with bands at 1640 and 1705 cm^{-1} (benzene solution) for the 1:1 adduct of acetone and boron trifluoride.⁷

Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{OBF}_3$: C, 55.60; H, 5.60; F, 26.39. Found: C, 55.73; H, 5.70; F, 26.33.

Mesitaldehyde-Hydrogen Bromide 2:1 Adduct. Dry hydrogen bromide was passed directly over 1.0 g. of neat mesitaldehyde. Deep yellow crystals formed immediately. These were triturated and then washed with dry hexane and collected by suction filtration. They melted at 40–50° dec. On standing in a desiccator the crystals evolved hydrogen bromide and in a few hours became oily.

The use of this procedure with hydrogen chloride gave a yellow oil, m.p. 8–12°, which rapidly evolved hydrogen chloride at room temperature.

Mesitaldehyde-Hydrogen Iodide 2:1 Adduct. Hydrogen iodide gas was passed over 0.6 g. of neat mesitaldehyde, yielding red-orange crystals. These were washed thoroughly with dry hexane, yield 0.3 g. They melted at 65–82° to a clear liquid which partly solidified at about 90° and remelted at 115–120° dec. On standing at room temperature in a desiccator the crystals decomposed to an oil mixed with red-brown crystals.

Mesitaldehyde-Perchloric Acid 2:1 Adduct. To a solution of 2.0 g. of mesitaldehyde in 3 ml. of glacial acetic acid was added 3 ml. of 70% perchloric acid. The resulting yellow crystalline precipitate was collected in a coarse sintered glass funnel protected from moisture and washed with cold acetic acid and then dry hexane. After being dried in a vacuum desiccator, the product weighed 2.4 g. Sublimation under 5 mm. pressure in a bath at 85° yielded 2.1 g. of a bright yellow sublimate, m.p. 138–140° dec. After two further sublimations the melting point was 148–149° (decomposition with gas evolution) and could be raised no further.

Anal. Calcd. for $C_{20}H_{23}ClO_3$: C, 60.52; H, 6.35; Cl, 8.95; mol. wt., 397. Found: C, 60.37; H, 6.18; Cl, 8.68; neut. equiv., 398.

Pyrolysis of the Adduct. The adduct (0.84 g.) was heated at 150° for 12 min. During this time the material melted and turned to a dark bubbling mass as a gas was evolved. A colorless liquid condensed on the upper walls of the reaction vessel and in the condenser. The reaction mixture was cooled and 2% aqueous sodium carbonate added. The carbonaceous residue was collected by suction filtration, 0.25 g. The benzene filtrate was dried and chromatographed over alumina. The benzene eluent yielded 0.2 g. (40% yield) of mesitylene as identified by its infrared spectrum.

Reduction of Mesitaldehyde-Perchloric Acid 2:1 Adduct. To a 1% solution of lithium aluminum hydride in ether was added a few milligrams of the 2:1 adduct. A vigorous reaction ensued with the formation of a colorless solution. After a few minutes, the

excess lithium aluminum chloride was decomposed with dilute hydrochloric acid. The crude reaction product was recovered by suction filtration. It melted at 87–88° and the melting point was undepressed when the substance was mixed with an authentic sample of mesitylcarbinol, m.p. 88–89°.

A hydrogenation was carried out as follows: a suspension of 0.33 g. of adduct and 0.25 g. of platinum oxide catalyst in 50 ml. of dry benzene was shaken at room temperature for 3 hr. under 1 atm. of hydrogen gas. A total of 620 ml. of hydrogen was absorbed. The mixture was filtered, washed with 5% sodium carbonate, and dried over magnesium sulfate. Removal of the solvent left 0.1 g. of white solid, m.p. 135–143°. Sublimation and recrystallization from hexane yielded 0.08 g., m.p. 148–149°. Mixing with an authentic sample of bis-2,4,6-trimethylbenzyl ether (m.p. 148–149°)¹² resulted in no depression in melting point.

Bis-2,4,6-trimethylbenzyl Ether from Mesitylcarbinol. To a solution of 0.3 g. of mesityl carbinol in 50 ml. of benzene was added 4 drops of 70% perchloric acid. The mixture was stirred for 3 hr. at room temperature, then decanted through filter paper. Concentration of the filtrate and recrystallization of the residue yielded 0.13 g. of bis-2,4,6-trimethylbenzyl ether,¹² m.p. 142–144°.

Reaction of Mesitaldehyde-Perchloric Acid 2:1 Adduct with Acetic Anhydride. A few milligrams of adduct was dissolved in a few milliliters of acetic anhydride and warmed gently on the steam bath for a few minutes. After chilling, the dark red solution was carefully poured into cold, concentrated potassium hydroxide solution. Acidification of the resulting solution gave a solid, and an oil having the odor of mesitaldehyde. The solid (yellow) was filtered and recrystallized from chloroform, m.p. 178–179°. The substance was soluble in dilute sodium bicarbonate solution and could be reprecipitated by the addition of dilute hydrochloric acid. The substance is believed to be *trans*-2,4,6-trimethylcinnamic acid (lit.¹³ m.p. 177.6–178°).

Similar treatment of the mesitaldehyde-perchloric acid 1:1 adduct (2 g.) with acetic anhydride led to an exothermic reaction on warming on the steam bath and the formation of 1.6 g. of a brown solid acid, m.p. 173–176°, identical with that obtained from the 2:1 adduct. No mesitaldehyde was detected.

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