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## RECOMMENDED METHODS FOR THE PURIFICATION OF SOLVENTS AND TESTS FOR IMPURITIES

### ACETONE

*Prepared for publication by*

J. F. COETZEE and T.-H. CHANG

Department of Chemistry,  
University of Pittsburgh, PA 15260, USA

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# Recommended methods for the purification of solvents and tests for impurities: acetone

Values are given for the most relevant physicochemical properties and solvation parameters of acetone. The most significant solvent properties of acetone, particularly the limitations imposed by aldol condensation, are discussed. Typical examples of electrochemical studies carried out in this solvent are listed. Methods are recommended for the purification of commercial acetone and for the determination of residual water and other impurities.

## INTRODUCTION

Acetone can be classified as a dipolar aprotic solvent although its protons are more reactive than those of typical members of this class of solvents. (This is also the case for nitromethane and, to some extent, for the formyl proton of dimethylformamide.) This proton reactivity constitutes the main limitation of acetone as a solvent. Other limitations are its exceptionally high hygroscopicity, high volatility and formation of explosive mixtures with air. On the credit side, acetone is available commercially in a sufficiently pure state for many (but not all) applications, it has a wide liquid range, a usefully low viscosity, and a relative permittivity (dielectric constant) that is sufficiently high to allow simple electrochemical measurements. Finally, its toxicity is low.

Physicochemical properties and solvation parameters of acetone are summarized in Table 1. The electron donor strength of acetone (as measured by its donor number of 17.0 with respect to antimony pentachloride as reference acid) is somewhat higher than those of the weakly basic dipolar aprotic solvents acetonitrile (14.1) and propylene carbonate (15.1) but well below those of the more basic solvents of this class, e.g., dimethylformamide (26.6) and dimethyl sulfoxide (29.8). As a result of its moderate electron donor strength, acetone is a fair solvent for inorganic substances, although its relative permittivity is sufficiently low that considerable ion association occurs. Acetone is an excellent solvent for many classes of organic compounds. Its exceptional solvent power for acetylene is utilized in the storage of acetylene. Acetone is also used commercially as a solvent for nitrocellulose (in the manufacture of explosives), cellulose acetate and many synthetic resins such as methacrylates. The principal commercial use of acetone, however, is in the manufacture of numerous chemicals, particularly such derivative solvents as methylisobutyl ketone (1).

Acetone has received less attention than many other dipolar aprotic solvents have as a medium for electrochemical and other solution chemistry studies. The most extensive investigations have been concerned with the conductance of electrolytes, although some voltammetric and potentiometric studies have also been carried out. The main results of these investigations are summarized below.

## KEY SOLVENT PROPERTIES OF ACETONE

### Proton acceptor and proton donor strength

Acetone is half protonated in 81.5% (by wt.) sulfuric acid (aq.) corresponding to a  $pK_a$  - value (aq.) of its conjugate acid of -7.2 (ref. 4); cf. acetonitrile, -9.5. The protons of acetone have considerable acidity,  $pK_a \sim 19$  (ref. 5), owing to the electron withdrawing properties of the carbonyl group and also the ease of charge delocalization from carbon to oxygen in the resulting carbanion.

### Solvating ability

Free energies of transfer of (mainly) alkali metal and halide ions have been estimated by means of a number of extrathermodynamic procedures. The probable validity of different procedures has been discussed by Marcus (ref. 6). As compared to the cyclic carbonyl compound, propylene carbonate, acetone appears to be a rather good solvator of the smaller alkali metal ions, in spite of its much lower relative permittivity which should weaken the electrostatic (Born) component of solvation. On the other hand, it appears to be a significantly weaker solvator of halide ions than propylene carbonate is.

TABLE I. Selected properties and solvation parameters of acetone

Freezing temperature, T/K -273.15 ( $t_m/^\circ\text{C}$ )	- 94.7
Boiling temperature at 101.325 kPa (1 atm), T/K -273.15 ( $t_b/^\circ\text{C}$ )	56.29
Flash point, $t_{f1}/^\circ\text{C}$	-18
Vapor pressure, p/kPa at 20°C	24.227
Density, $\rho/\text{kg dm}^{-3}$	0.78440
Dynamic viscosity, $\eta/\text{mPa s}$	0.3040
Surface tension, $\gamma/\text{mN m}^{-1}$ , at 20°C	23.32
Enthalpy of vaporization, $\Delta H_v/\text{kJ mol}^{-1}$ , at $t_b$	29.09
Molar heat capacity, $C_p/\text{J K}^{-1} \text{mol}^{-1}$ , at 30°C	129.2
Refractive index, $n_D$	1.35596
Dipole moment, $\mu/D$ , in hexane at 20°C	2.69
Relative permittivity (dielectric constant), $D = \epsilon/\epsilon_0$	20.70
Donor number (Gutmann), DN/kcal mol <sup>-1</sup> <sup>a</sup>	17.0
Acceptor number (Mayer-Gutmann), AN/dimensionless	12.5
Solvatochromic parameters (Kamlet-Taft)	
-- polarity parameter, $\pi^*$	0.72
-- hydrogen bond acceptor parameter, $\beta$	0.48
-- hydrogen bond donor number, $\alpha$	(0.07) <sub>b</sub>

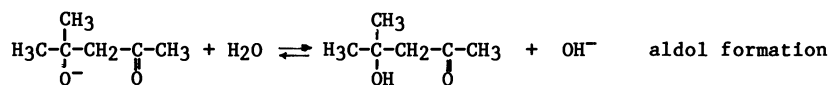
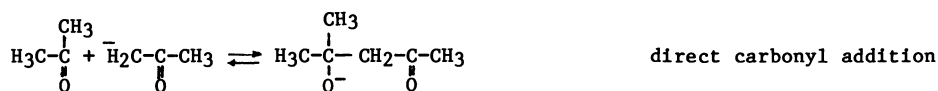
Values of properties are from Ref. 1 and are for 25°C, except where otherwise noted. Donor and acceptor numbers are from Ref. 2 and solvatochromic parameters are from Ref. 3; values are for 25°C.

<sup>a</sup> 1 cal = 4.184 J

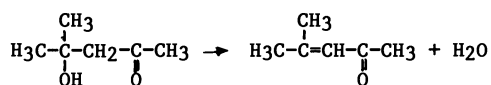
<sup>b</sup> Somewhat uncertain; see Ref. 3.

### Enolization and aldol condensation

Acetone exists as a keto-enol tautomeric equilibrium mixture containing ca. 10<sup>-4</sup>% of the enol form, as determined by bromometric titration (ref. 7). It is to be noted that the enol concentration is too low to be observed in spectrophotometric or relaxation experiments, which are applicable to such other carbonyl compounds as  $\beta$ -diketones in which the enol content is much higher. The principal limitation of acetone as a solvent is the ease with which it undergoes aldol condensation, which is both acid and base catalyzed. These reactions have been extensively studied (ref. 4, 5, 7). Base catalysis occurs as follows.

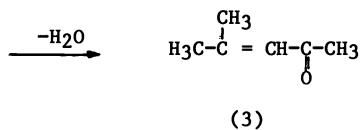
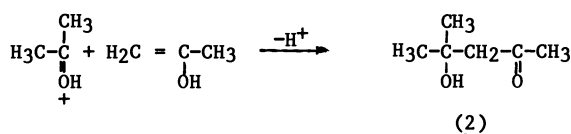
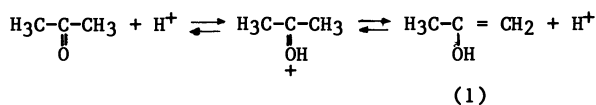


The product, 4-hydroxy-4-methyl-2-pentanone, is easily dehydrated (e.g., by Lewis acids), forming the very stable 4-methyl-3-penten-2-one (mesityl oxide):



This series of reactions is of extreme importance in, among other things, the purification of acetone. Many commonly used desiccants are sufficiently basic (or acidic) to cause aldol condensation. For example, Riddick (ref. 1) found an increase in the water content of acetone after treatment with alumina, which acts as a mild desiccant in other solvents. In fact, deliberate condensation of liquid ketones can be accomplished by adsorption on basic alumina at room temperature (ref. 8).

Acid catalysis of aldol condensation probably occurs via the enol tautomer (1) to form an unstable  $\beta$ -hydroxy ketone (2) which then rapidly undergoes acid-catalyzed dehydration to the very stable mesityl oxide (3).



Further condensation may also occur. For example, in presence of hydrogen chloride not only mesityl oxide, but also phorone,  $(\text{CH}_3)_2\text{C}=\text{CH}-\text{C}=\text{CH}=\text{C}(\text{CH}_3)_2$ , is formed, while in presence of sulfuric acid 1,3,5-trimethylbenzene,<sup>0</sup>mesitylene, is produced. This instability of solutions of especially the stronger acids in acetone is obviously a serious limitation of this solvent.

### TYPICAL ELECTROCHEMICAL STUDIES IN ACETONE

Acetone was one of the many solvents included in the early, extensive conductometric studies of salts by Walden, which also included methylethyl ketone (ref. 9), and by Kraus (ref. 10). It was found that many alkali metal and tetraalkylammonium salts have ion pair formation constants in the range  $10^2 - 10^3 \text{ L mol}^{-1}$ . The polarography of the lanthanide metal ions, sodium, potassium and rubidium ions, and other inorganic substances has been studied by Coetzee and Siao (ref. 11), while Gutmann et al. (ref. 12) investigated all alkali metal ions and thallium(I) ion. The half-wave potentials were compared with similar data for a variety of other solvents by Coetzee et al. (ref. 13) and by Gritzner (ref. 14). Overall, acetone behaves as a differentiating solvent as compared to water. The electroreduction of such acidic solutes as the lanthanide metal ions is complicated by hydrogen evolution, either from residual water or from acetone itself.

Many potentiometric acid-base titrations have been carried out in acetone, which behaves as a typical differentiating solvent in such applications; it should be reiterated, however, that solutions of many acids and bases in acetone are not ideally stable owing to aldol condensation (v.s.). Titration and other results obtained in acetone have been summarized by Charlot and Trémillon (ref. 15).

### MANUFACTURE OF AND IMPURITIES IN ACETONE

Until World War I, acetone was manufactured by dry distillation of calcium acetate, obtained by neutralizing pyroligneous acid (from wood distillation) with lime. The greatly increased demand for acetone as a solvent for nitrocellulose-based explosives led to the development of the Weizmann process involving fermentation of starch (later: molasses) by means of the bacillus clostridium acetobutylicum. The Weizmann process, in

turn, was displaced by catalytic dehydrogenation of 2-propanol (using copper or various metal oxides as catalysts) and, to some extent, by several other synthetic processes. Commercial acetone is now relatively pure, with water as the main impurity. The ACS specifications for reagent grade acetone (ref. 16) include the following: density  $< 0.7857 \text{ kg dm}^{-3}$  at  $25^\circ\text{C}$ ; water  $< 0.5\%$  (by wt.); methanol and 2-propanol  $< 0.05\%$ ; aldehydes (as HCHO)  $< 0.002\%$ ; titratable acid (1:1 by vol. acetone-water mixture titrated with NaOH to phenolphthalein end point)  $< 3 \times 10^{-4} \text{ mol OH}^- \text{ kg}^{-1}$  acetone; titratable base (ca. 1:1 by vol. acetone-water mixture titrated with HCl to methyl red end point)  $< 6 \times 10^{-4} \text{ mol H}^+ \text{ kg}^{-1}$  acetone.

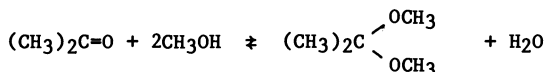
## PURIFICATION OF ACETONE

The relatively high purity of commercial acetone is an obvious advantage. On the other hand, the ease with which acetone undergoes either acid- or base-catalyzed aldol condensation complicates any additional purification. Removal of the main impurity, water, presents a problem because even such mildly acidic or basic desiccants as silica gel or alumina cause aldol condensation (v.s.). Riddick (ref. 1) found that drying with anhydrous calcium sulfate (Drierite) followed by careful fractional distillation is most effective, although it is difficult to lower the water content of this very hygroscopic solvent below  $10^{-2} \text{ M}$ . Coetzee and Siao (ref. 11, 17) used a related method which is described below.

Dry the acetone by shaking with Drierite ( $25 \text{ g L}^{-1}$ ) for several hours. Decant and distill from fresh Drierite ( $10 \text{ g L}^{-1}$ ) through an efficient column, e.g., a Stedman column. Maintain contact with the atmosphere through a Drierite drying tube. (**Caution:** Do not use anhydrous magnesium perchlorate which may explode in contact with acetone vapor.) Store the distillate in a dark container fitted with a siphon for dispensing the solvent.

## TESTS FOR RESIDUAL IMPURITIES IN ACETONE

Conventional Karl Fischer titration of water in acetone (and other active carbonyl compounds) produces a drifting end point and serious overtitration owing to (slow) generation of additional water as a result of ketal formation:



The problem is aggravated by the relatively slow reaction of Karl Fischer reagent with water. Better results are obtained with recently introduced modifications of Karl Fischer reagent in which pyridine is replaced by sodium acetate (ref. 18) or ethanolamine (ref. 19) and which react faster with water. At least one preparation is available commercially as J. T. Baker Chemical Company ReAquant reagent. An automated stopped-flow determination of water in acetone utilizing this reagent has been described (ref. 20). Further improvement has been claimed when methanol is replaced by a chloroform-methanol mixture as titration medium (ref. 21). The following procedure was recommended for acetone containing 0.2% water; appropriate adjustments in volumes may be necessary for lower water concentrations.

Pretitrate 4–5 mL of 2:1 (by vol.) chloroform-methanol with Karl Fischer reagent containing ethanolamine, using preferably the "dead-stop" method for equivalence point detection. Inject 100  $\mu\text{L}$  of acetone and record volume of reagent used as a function of time for a sufficient length of time (up to a few minutes) to allow satisfactory extrapolation of the (relatively flat) line to zero time.

Various other methods for the determination of water in acetone have been proposed. These methods are reviewed in ref. 17. The infrared absorption band of water at  $2.70 \mu\text{m}$  can be used for water concentrations greater than 0.01%. Water can also be determined by adding excess acetyl chloride and titrating the acetic acid liberated, or by adding excess calcium hydride and measuring the volume of hydrogen liberated as a function of time, extrapolating to zero time to allow for the reaction of calcium hydride with acetone itself (ref. 11, 17). It appears, however, that in general the modified Karl Fischer titration described above is to be preferred.

### DETERMINATION OF OTHER IMPURITIES

The density and refractive index, as well as the differential boiling-condensing temperature (ref. 1), are useful criteria for contamination in general.

Methanol and 2-propanol can be determined by gas chromatography or by their reducing action on permanganate ion, and aldehydes can be determined by the Schiff-Villavecchia reaction (ref. 1).

Electroactive impurities can be determined voltammetrically. The polarographic window of acetone at the dropping mercury electrode with tetraethylammonium perchlorate as supporting electrolyte extends from +0.58 to -2.46 V vs. SCE(aq.); the cathodic limit appears to be determined by reduction of acetone itself (ref. 17).

### ULTRAVIOLET CUTOFF

For a typical commercial reagent grade of acetone (intended for spectrophotometry), maximum absorbances (in a 1-cm optical cell) are specified as 1.00 at 330 nm and 0.10 at 340 nm.

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