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Ketene Lamp

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Abstract

Ketene (H_2CCO) is a versatile reagent in organic chemistry that can be used to create a variety of other organic species, including anhydrides, carboxylic acids, esters, amides, allenes, and strained cyclic ketones. Unfortunately, it cannot be purchased or transported due to its acute inhalation toxicity. Ketene must be generated at the point of use and stored for only a short period of time. A ketene lamp is a convenient and reliable method of ketene production by the cracking of acetone, a cheap and widely available organic solvent. This article explains the construction of a ketene lamp from readily available components and its safe operation to generate ketene or other pyrolysis products.

Background

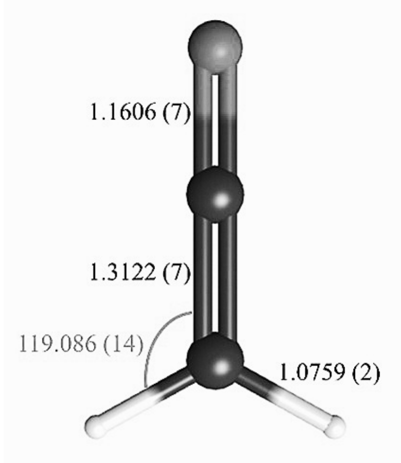

Figure 1. *Ketene structure.*[1] *Semi-experimental equilibrium structure (r_e^{SE}) of ketene with 2σ statistical uncertainties from least-squares fitting of the moments of inertia from 16 isotopologues. Distances are in angstroms and the angle is in degrees.*

Chemical Formula	**C_2H_2O**
Molar Mass	**42 g/mol**
Melting Point	**-150°C**
Boiling Point	**-56°C**
CAS # 463-51-4	
IUPAC Name : Ethenone	

Table 1. *Ketene information*[2]

Ketene ($H_2C{=}C{=}O$) is the simplest member of the family of compounds that collectively are known as ketenes which contain the CCO functional group.[3] Compounds in this family are generally highly reactive towards cycloadditions and additions of nucleophiles to the central carbon atom. Because of their reactivity, ketenes are useful starting materials for the production of anhydrides, carboxylic acids, esters, amides,

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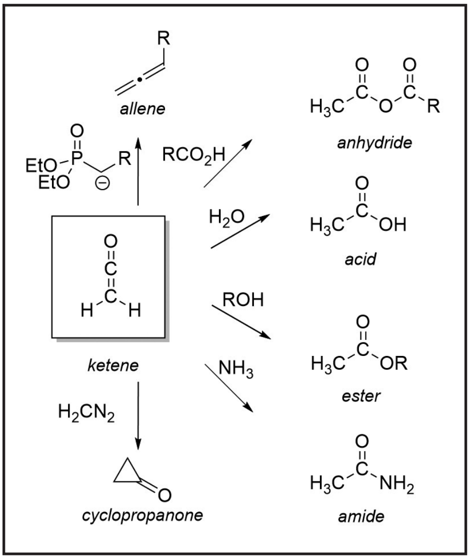
[1] H. H. Smith, B. J. Esselman, S. A. Wood, J. F. Stanton, R. C. Woods & R. J. McMahon, "Improved Semi-experimental Equilibrium Structure and High-level Theoretical Structures of Ketene," *The Journal of Chemical Physics* 2023, 258 (24): 244304.

[2] W. M. Haynes, *CRC Handbook of Chemistry and Physics* (Boca Raton, FL: CRC Press, 2014): section 3: 336, section 5: 21 & 24.

[3] T. T. Tidwell, *Ketenes* (Hoboken, New Jersey: John Wiley & Sons, 2005): 55-625.

and even more difficult to produce functional groups such as allenes and cyclopropanones (Scheme 1).[3]



Scheme 1. *Reactions of ketene with various nucleophiles*

In addition to synthetic organic chemistry,[3,4] the ketene family is important to many diverse areas of science including petroleum refining,[5] photolithography,[6] atmospheric chemistry,[7] combustion,[8] and astrochemistry.[9] Ketene (H_2CCO) has been identified as an interstellar molecule first within our Milky Way galaxy in Sagittarius B2,[10] and later in extra-galactic sources.[11]

As useful and interesting as ketene is, it is not commercially available. Of particular concern is its acute inhalation toxicity. The amount of ketene that is considered Immediately Dangerous to Life or Health (IDLH) is only 5 parts per million (ppm), making it as dangerous as phosgene.[12] Use of ketene necessitates caution, appropriate safety measures, and qualified personnel experienced in the manipulation of toxic gases. Because of these safety concerns, ketene must be generated at the point of use, and stored for only short periods. The use of a ketene lamp is a convenient and reliable method of ketene production from cheap and widely available acetone. The ketene lamp presented here is a modification of a design by Hurd and coworkers,[13] and can be used in any facility equipped to safely study or utilize ketene.

At the University of Wisconsin-Madison, we recently used our ketene lamp extensively to

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[4] C. Wentrup, "Three Carbon-Heteroatom Bonds: Ketenes and Derivatives," *Science of Synthesis* (Stuttgart, Germany: Georg Thiema Verlag, 2006): Vol. 23.

[5] Y. Zhang, P. Gao, F. Jiao, Y. Chen, Y. Ding, G. Hou, X. Pan & X. Bao, "Chemistry of Ketene Transformation to Gasoline Catalyzed by H-SAPO-11," *Journal of the American Chemical Society* 2022, 144 (40): 18251-18258.

[6] F. A. Leibfarth & C. J. Hawker, "The Emerging Utility of Ketenes in Polymer Chemistry," *Journal of Polymer Science Part A: Polymer Chemistry* 2013, 51 (18): 3769-3782.

[7] M. J. Newland, G. J. Rea, L. P. Thüner, A. P. Henderson, B. T. Golding, A. R. Rickard, I. Barnes & J. Wenger, "Photochemistry of 2-Butenedial and 4-Oxo-2-pentenal Under Atmospheric Boundary Layer Conditions," *Physical Chemistry Chemical Physics* 2019, 21 (3): 1160-1171.

[8] W. Sun, J. Wang, C. Huang, N. Hansen & B Yang, "Providing Effective Constraints for Developing Ketene Combustion Mechanisms: A Detailed Kinetic Investigation of Diacetyl Flames," *Combustion and Flame* 2019, 205: 11-21.

[9] R. L. Hudson & M. J. Loeffler, "Ketene Formation in Interstellar Ices: a Laboratory Study," *The Astrophysical Journal* 2013, 773 (2): 109.

[10] B. Turner, "Microwave Detection of Interstellar Ketene," *The Astrophysical Journal* 1977, 213: L75-L79.

[11] S. Muller, A. Beelen, M. Guélin, S. Aalto, J. H. Black, F. Combes, S. J. Curran, P. Theule & S. N. Longmore, "Molecules at z = 0.89," *Astronomy & Astrophysics* 2011: 535, A103.

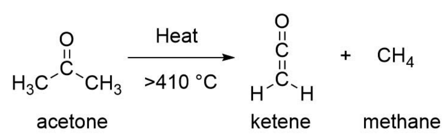
[12] M. E. Barsan, *NIOSH Pocket Guide to Chemical Hazards* (Cincinnati, Ohio: NIOSH Publications, 2007): 215 & 253.

[13] J. W. Williams & C. D. Hurd, "An Improved Apparatus for the Laboratory Preparation of Ketene and Butadiene," *The Journal of Organic Chemistry* 1940, 5 (2): 122-125.

determine an improved semi-experimental equilibrium structure for ketene.[1] This work required ketene samples with no impurities detectible to our rotational spectrometer, and the preparation of ketene's deuterium isotopologues, HDCCO and D_2CCO. Here we detail the construction and operation of a ketene lamp, and how this apparatus can be used to create other pyrolysis products.

Acetone Pyrolysis

Ketene is produced when acetone is cracked or heated in an environment without oxygen which generates methane as a co-product (Scheme 2). Acetone is very stable and will not generate ketene at ambient conditions, but at higher temperatures (>410°C), ketene and methane are more stable than acetone. Thus, as the temperature is increased in conditions where combustion is not possible, acetone decomposes to produce methane and ketene. This can be rationalized by the temperature dependence of the Gibbs free energy ΔG° equation (Table 2 and Figure 2). At low temperatures, the large negative value of the enthalpy (ΔH°) of acetone prevents it from decomposing, but at high temperatures the entropy (ΔS°) term overtakes the stability of acetone and allows ketene and methane to dominate the equilibrium.



Scheme 2. *Pyrolysis of acetone*

Ketene Lamp Design and Construction

The ketene generator shown in Figure 3 consists of two pieces:

- the main pyrolysis chamber
- the heating lamp insert

	$\Delta_f H°$ kJ/mol	$\Delta_f G°$ kJ/mol	S° J/mol K	C_P J/mol K
Ketene	-47.5	-48.3	247.6	51.8
Methane	-74.6	-50.5	186.3	35.7
Acetone	-217.1	-152.7	295.3	74.5

Table 2. *Thermodynamic information*[2]

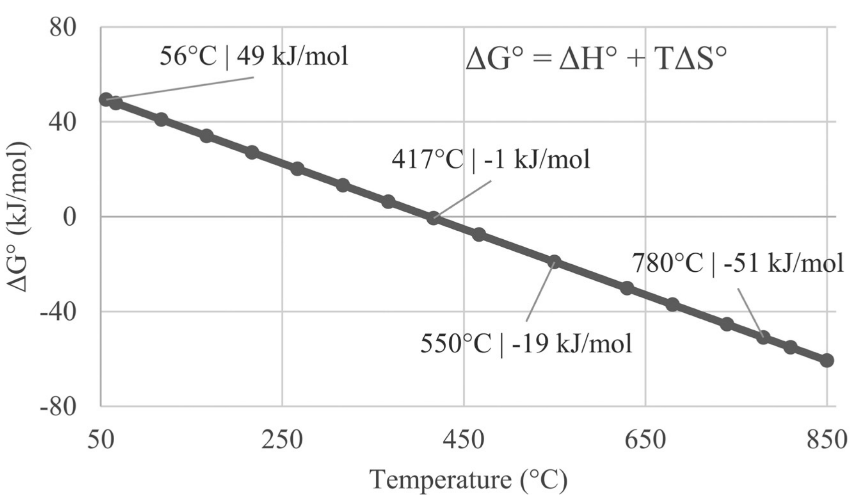


Figure 2. *Gibbs free energy of acetone pyrolysis*

The bottom of the pyrolysis chamber is a 24/40 inner joint that connects to a boiling flask, this flask conveys the acetone vapor up to the heating filament that is inserted into the top 40/50 outer joint of the chamber. The heating filament is held by an 8 mm glass rod which is attached to the sealed-off bottom of a 40/50 inner joint. Two tungsten wires (Kuhlgrid) are sealed through the glass via a glass-to-metal seal. These wires are spot welded to both ends of a loop of nichrome wire to make up the heating element. The 22-gauge nichrome wire is roughly 3 meters long with a 10-ohm resistance. The nichrome wire loop is loosely coiled and supported by the glass rod, two glass support struts, and a glass loop at the end of the rod. The braided Kuhlgrid wires inside the 40/50 inner joint are fed through 3 mm glass tubes. A rubber stopper keeps them electrically isolated from each other and acts as a cable grommet. Figure 4 shows the heating lamp insert.

The side 24/40 outer joint connects to a water-cooled condenser, which condenses acetone that then drips back down into the boiling flask through a side arm with a U-bend. The U-bend acts as a vapor-lock preventing vapor from bypassing the heating filament.

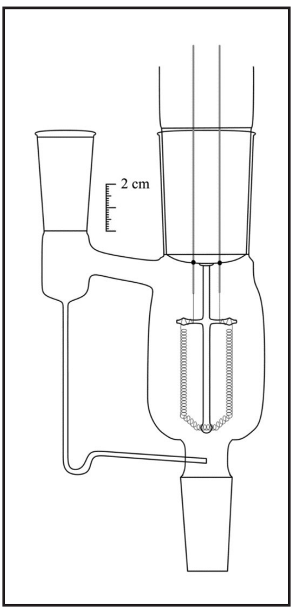


Figure 3. *Ketene generator dimensional schematic*

Figure 4. *Heating lamp insert*

Construction of Pyrolysis Chamber

Construction of the pyrolysis chamber begins with a 40/50 outer joint that is fire cut at 30 mm length from the joint, this is then sealed onto 58 mm diameter standard walled tubing. At a length 75 mm from that seal, the 58 mm tubing is pulled down in preparation for the next seal. The closed end of the 58 mm tubing is opened enough to be sealed onto a pre-prepared 35 mm long 24/40 inner joint, as shown in Figure 5.

Figure 5. *Assembly of main body*

Next, in preparation for a seal onto the pyrolysis chamber, a point is pulled on a 28 mm diameter standard walled tube and it is cut at 50 mm length then peeled to a 105 degree angle. The peeled end of that prepared tube is sealed to the pyrolysis chamber below the 40/50 outer joint before being flame annealed. The through seal tube is prepared. A point is pulled on the end of a 9 mm medium walled tube. A maria is pushed 50 mm down from the point. A drip tip on the other end is measured from the maria, then is cut and ground. This is ring-sealed through the middle of the 24/40 inner joint tubing of the main body, with the internal part of the 9 mm tube hitting the centerline axis of the main body. The construction is flame annealed. This stage is shown in Figure 6.

The next portion prepared for attachment is the 24/40 inner joint side-arm assembly. A 24/40 inner joint is pulled down to form

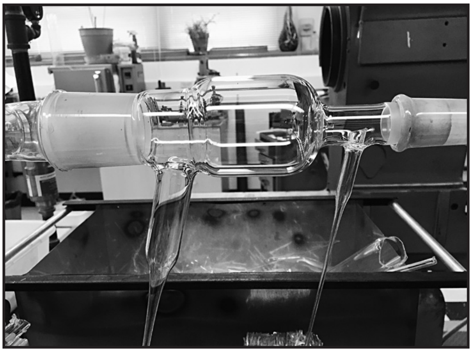


Figure 6. *Side seal and through-seal on main body*

a 50 mm round bottom. A hole is popped, and a straight seal is used to attach 300 mm of 9 mm medium walled tube. A U-bend is prepared by setting the joint tube at the half-way point on the 22 mm side seal tube and a mark is made on the 9 mm tube at the top of the 24/40 inner joint of the main body. The U-bend is made at this mark, as shown in Figure 7. While the U-bend glass is still hot,

Figure 7. *U-bend*

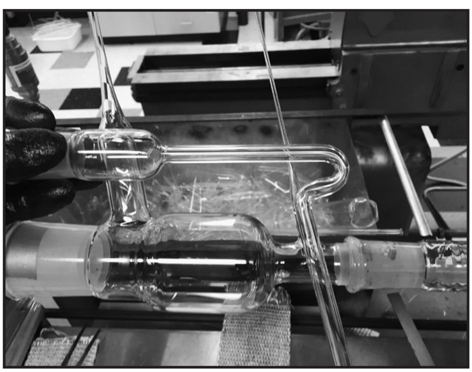


Figure 8. *Completed side arm assembly before sealing*

the assembly is positioned adjacent to the pyrolysis chamber, and a mark is made on the 9 mm tube where it crosses the pointed end of the 9 mm side seal. A 105 degree bend is made at that marking as shown in Figure 8.

Next, the side arms off the main body are prepared to be joined to the side arm assembly as shown in Figure 9. The 22 mm side-arm tube is marked at 30 mm from the main body, then is cut and peeled. The 9 mm tube is cut and peeled to be even with the outer diameter of the 58 mm tube.

Figure 9. *Prepared side arms off the main body*

The side arm assembly is aligned with the main body. The main body is used as a guide to mark an appropriate length past the second bend in the 9 mm tube, then at that mark, the 9 mm tube is cut and peeled. Next a hole is blown in the 24/40 tubing on the side arm assembly. Figure 10 shows the prepared pieces before sealing.

Figure 10. *Prepared pieces before sealing*

The final step in the construction of the pyrolysis chamber is a delicate double stick seal that joins the side arm assembly to the main body. There are multiple aspects of this process that can go wrong; proper execution requires the utmost attention to every detail before this operation is attempted. Diligently, preparations are made in advance. The workspace is arranged to have a pick and clean small diameter rod readily accessible. The diameter of each opening is verified, so too is the fit, level, and alignment. By design, these final seals take place off the main body to mitigate the risk of cracking.

After all preparations are made, the 22 mm tube opening and side arm opening are heated and are then rocked forward from the bottom of the 24/40 joint – left to right. Next, while heating the front and back sides of the 22 mm and the 9 mm openings, the 9 mm tubes are sealed together. Heat is applied as needed to align and level in all directions. Afterwards the seals are cleaned up, alternating in quarters between the 22 mm and 9 mm tubes. After these are sealed, cleaned up, the alignment verified, and flame annealed, the U-bend area is cleaned up as needed. The completed pyrolysis chamber is shown in Figure 11.

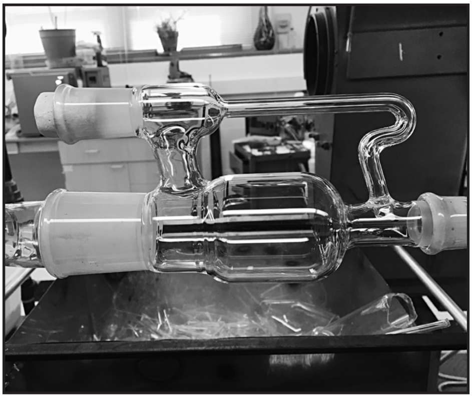


Figure 11. *Completed pyrolysis chamber body*

Ketene Lamp Usage

The information in this article alone is insufficient to responsibly generate ketene; readers are directed to the cited document for a freely available introduction into laboratory safety.[14] There are several ways to utilize ketene, and some do not require the ketene to be pure. Here we will detail how to obtain and purify ketene; this requires additional glassware beyond the ketene lamp (Figure 12).

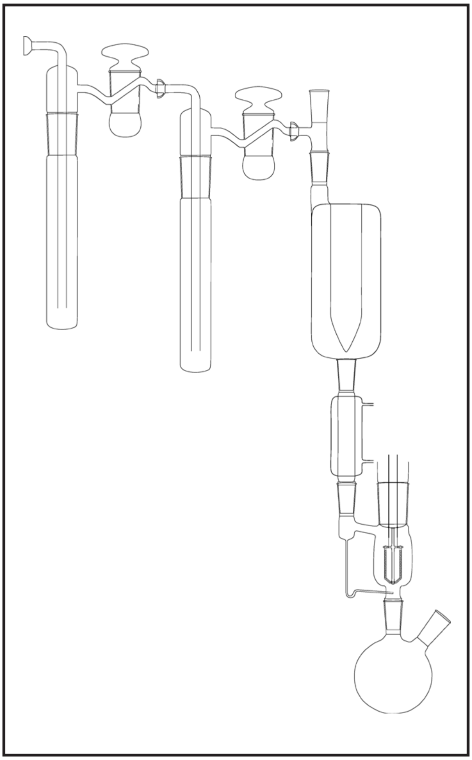


Figure 12. *Drawing of glassware used for the production and purification of ketene*

First, the glass components of the full ketene apparatus (Figure 13) are assembled, placed under vacuum, and the entire apparatus is thoroughly inspected. The valve on the first cold trap (Figure 13 #9) is closed. Through the valve (Figure 13 #8) above the cold finger (Figure 13 #6), dry nitrogen gas is introduced into the apparatus to create an inert atmosphere, leaving this valve open to nitrogen and a mineral oil

[14]National Research Council, *Prudent Practices in the Laboratory: Handling and Management of Chemical Hazards*,updated version (Washington, DC: The National Academies Press, 2011).

bubbler. The glass stopper (Figure 13 #1) is removed and 200 mL of HPLC grade acetone and a Teflon® stir bar are added to the two-neck round-bottom flask (Figure 13 #2), then the stopper is returned to the flask. A flow of water through the water-cooled condenser (Figure 13 #5) is started. The two-neck round-bottom flask (Figure 13 #2) is heated, bringing acetone to a vigorous reflux, which is maintained for a minimum of one hour.

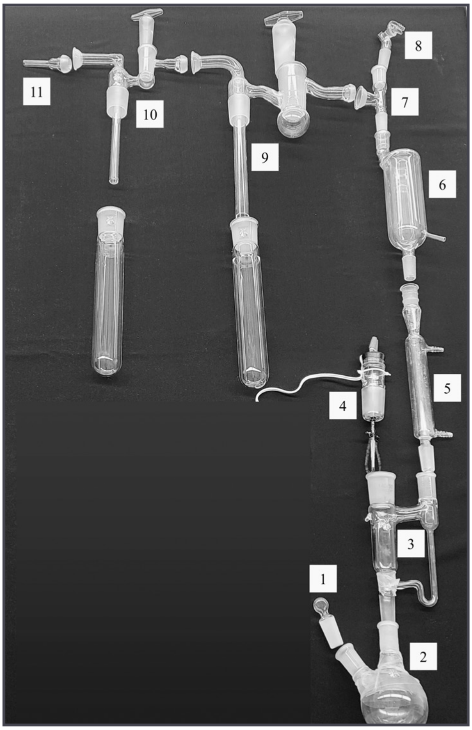


Figure 13. *Ketene isolation apparatus Photo of glassware used for the production and purification of ketene*

1. *24/40 glass stopper*
2. *two-neck 250-mL round-bottom flask*
3. *pyrolysis chamber*
4. *custom pyrolysis insert with nichrome wire*
5. *24/40 taper water-cooled condenser*
6. *24/40 taper cold finger trap*
7. *three-way adaptor*
8. *24/40 inner to hose barb with glass valve*
9. *taper cold trap and high-vacuum valve*
10. *cold traps and high-vacuum valve*
11. *35/20 ball to 3/8 in. open tube*

Dry ice/acetone is added to the cold finger (Figure 13 #6) and the Dewar flask at the first cold trap (Figure15 #9). A *n*-pentane/liquid nitrogen slurry is added to the Dewar flask at the second cold trap (Figure 13 #10). Through the ultra-torr glass adaptor (Figure 13 #11), dry nitrogen gas is introduced to both cold traps; positive pressure of nitrogen is maintained with an oil bubbler. A second close inspection of the apparatus is conducted for any glassware flaws. The glass valve on the first cold trap (Figure 13 #9) is opened, and the valve on the hose-barb adaptor (Figure 13 #8) is closed. The heating element (Figure 13 #4) is connected to a variable current power supply equipped with an ammeter, and the current is slowly ramped. We found that 6.5 amps worked best for our apparatus, but appropriate amperage should be determined separately for each lamp. When the heating element (Figure 13 #4) is hot enough to generate ketene, an opaque white vapor is visible in the cold finger trap (Figure 13 #6); if this is not observed, the current may need to be increased. The heating element (Figure 13 #4) should glow a dull cherry red color as shown in Figure 14,

Figure 14. *Ketene lamp while in use*

and vapor should condense on the cold finger (Figure 13 #6).

The flow of nitrogen gas through the ultra-torr adaptor (Figure 13 #11) can periodically be suspended; when nitrogen is not flowing, any bubbling observed in the oil bubbler is caused by the more highly volatile products (e.g., methane) being produced. If gas production observed at the nitrogen oil bubbler stops, the reaction should be shut down. The reaction is monitored for three hours or until a sufficient quantity of ketene has been generated. The residual solvent in the boiling flask gradually turns from colorless to yellow (as seen in Figure 14), then orange, and eventually black. The level of acetone in the boiling flask (Figure 13 #2) slowly decreases throughout the reaction and is monitored. If soot formation is observed, the heating element (Figure 13 #4) is too hot. If vapor condensation on the cold finger ceases (Figure 13 #6), or if the level of acetone in the boiling flask (Figure 13 #2) gets too low, the reaction is shut down.

After the ketene has been collected in trap 2, the heating element (Figure 13 #4) is turned off, and the apparatus is monitored for another 15-30 minutes or until the white vapor is no longer visible. The valve on the hose barb adaptor (Figure 13 #8) is opened, and the glass valve on the second cold trap (Figure 13 #10) is closed. While still at −130°C, the second cold trap is intermittently subjected to vacuum until the static vacuum pressure in the second cold trap is approximately 3 torr. The pure ketene is then vacuum transferred to a stainless-steel holding vessel for storage and use. This procedure can be used to generate > 10 g of ketene per hour.

Other Pyrolysis Applications

The ketene lamp can be used for other pyrolysis reactions, but the exact procedure must be modified for each specific pyrolysis process. The main variables to adjust are 1) the starting material, 2) the pyrolysis temperature, 3) separation temperatures, and 4) vacuum distillation final pressure. The choice of starting material is fundamentally intrinsic to the reaction and depends on the desired product. Calculations similar

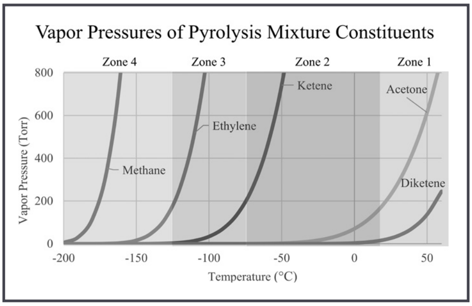


Figure 15. *The four temperature stages used for ketene purification*

Zone 1 : ~10°C
Cooled by tap water flowing through the water jacketed condenser (Figure 13 #5).

The majority of unpyrolyzed acetone is condensed then returns to the boiling flask. Less volatile impurities are removed at this stage, such as diketene, acetic acid, and acetic anhydride.

Zone 2 : -78°C
Cooled by dry ice acetone baths in the cold finger and the Dewar around the first cold trap (Figure 13 #6 & #9).

All remaining acetone and other less volatile impurities are removed at this stage; some acetone is condensed by the cold finger, and the rest is caught in the cold trap. Some ketene is caught at this stage too.

Zone 3 : -130°C
Cooled by a n*-pentane slurry in a Dewar around the second cold trap (Figure 13 #10).*

Nearly all ketene remaining in the vapor mixture is caught in this cold trap, while methane continues past. Some ethylene is collected with the ketene, a subsequent vacuum distillation is necessary to remove this ethylene.

Zone 4 : Room Temperature
At this stage, the remaining vapor mixture (mostly methane) is vented through an oil bubbler into the back of a fume hood. Alternatively, the mixture could be bubbled through water to remove the trace amounts of ketene. Positive nitrogen pressure is maintained in this region with a bubbler to prevent atmospheric contamination via back flow.

to those shown in Figure 2, and the observables, such as soot formation already described in the acetone pyrolysis procedure, demonstrate how pyrolysis temperature can be determined.

Optimal separation temperatures are chosen after identifying the constituents of the pyrolysis mixture and their vapor pressures. Figure 15 shows the vapor pressures of various substances found in the acetone pyrolysis mixture, and the separation temperatures used in the purification of ketene. Designing these types of procedures is an iterative process, some details are optimized empirically. For example, the ketene purification uses both a cold finger and cold trap at -78°C because acetone was observed to contaminate the ketene if only the cold finger was used.

The last variable, vacuum distillation final pressure, is the observed vapor pressure of the pyrolysis product when it is free of other contaminants. The pressure will depend on the temperature of the final cold trap used, and the final pressure can be looked up if the vapor pressure curve for the compound has been reported in the literature. In practice, the observed pressure will depend on the specific equipment used, so this parameter is also found empirically.

Conclusion

Ketene (H_2CCO) is a synthetically useful compound that likely will never be commercially available due to the difficulty of transportation and storage. A ketene lamp can be constructed from widely available and inexpensive materials and can be used to make ketene (H_2CCO) on demand. The lamp can also be used to make other compounds through pyrolysis, such as methyl ketene made from propionic anhydride.[15] In principle, this apparatus could be used for the pyrolysis of most materials with sufficient vapor pressure, and with current increased interest in pyrolysis research for chemical recycling,[16] the ketene lamp might fill a valuable niche for cheap laboratory scale pyrolysis.

Acknowledgments

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[15] A. Jenkins, “The Preparation and Dimerization of Methylketen,” *Journal of the Chemical Society (Resumed)* 1952: 2563-2568.

[16] L. Dai, N. Zhou, Y. Lv, Y. Cheng, Y. Wang, Y. Liu, K. Cobb, P. Chen, H. Lei & R. Ruan, “Pyrolysis Technology for Plastic Waste Recycling: A State-of-the-art Review,” *Progress in Energy and Combustion Science* 2022, 93, 101021.