Formation of Small Organic Acids During ENDS Aerosol Collection

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Abstract

To reduce the risks associated with combustible nicotine products, efforts have focused on the production of non-combustible alternatives such as electronic nicotine delivery systems (ENDS). At the 75th TSRC, we presented our findings into potential ketene generation through thermal degradation of ester flavorants during ENDS aerosol generation.[1] As part of this, we observed the creation of products formed from reactive species generated by propylene glycol (PG) and glycerol (VG), speculating that these species may have been small organic acids (SOA). Here we present our findings in a study looking at SOA generation from PG, VG, and select ester flavorants.

Model e-liquids were vaped under regular-to-moderate experimental conditions (0.7–1.8 Ω coils, 12–75 W power setting, 55/3/30 puff regime) using the CORESTA recommended device (Aspire Nautilus™ tank system with an Evolv™ Reference Mod DNA 75 Color battery, collected in puff blocks to dryness, and analyzed using ion chromatography. Generally, the amount of SOA produced was dependent on the power setting and collection duration/puff block. Initial results showed that PG and VG both contributed to the formation of acetic acid (0.112–8.07 µg/puff & 0.207–86.3 µg/puff, respectively) and formic acid (0.122–0.713 µg/puff & 0.229–5.43 µg/puff respectively). VG was shown to be primarily responsible for the formation of propionic acid (ND–11.2 µg/puff). At higher power settings, acrylic acid was also observed at levels up to 2.46 µg/puff along with conversion of ester flavorants to their corresponding acid to varying degrees. The initial study, was expanded to include a systematic analysis of the thermal breakdown products associated with PG and VG using two different devices and multiple power settings. Though not on the FDA's published HPHC list, these acids have associated hazards that warrant further investigation into their production and effects of long-term exposure.

Study Overview

- E-liquids are comprised primarily of propylene glycol (PG) and glycerol (VG), nicotine, and flavorings.
- High energy and heat put into system can thermally degrade PG and VG into various small organic acids.
- Possible small organic acids:
  - Formic acid, acetic acid, propionic acid, lactic acid, acrylic acid, pyruvic acid.
- Though not found to be carcinogenic, these acids are irritants with associated hazards which warrant further investigation.

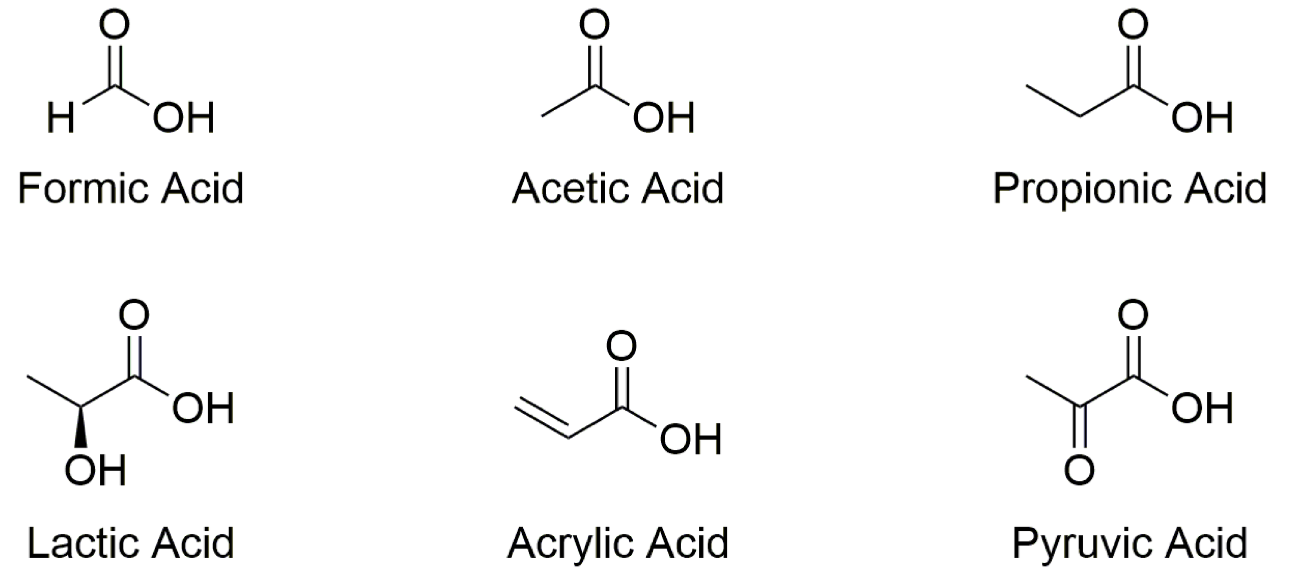


Figure 1. Possible small organic acids produced during the vaping process.

Methodology

- Model e-liquids were prepared:
  - PG
  - VG
- Vape conditions (volume/duration/frequency): 55/5/30
- Battery and tanks used:
  - Evolv™ Reference Mod DNA 75 Color with Nautilus™ Mini tanks[2]
  - Smok™ RPM 40 Device
- Samples were smoked with coil resistances of 0.8 Ω (Smok™) and 1.6 Ω Nautilus™.
- Power settings on batteries ranged from 10 W to 40 W (Smok™) and 12 W to 50 W (Nautilus™).
- Samples collected in two puff blocks:
  - First block collected as "wet puffs" only
  - Samples collected to dry/burnt-puffing conditions
- Samples collected into micro-impinger containing 10 mL of water cooled in an ice water bath.
- Analysis performed using ion chromatography with suppressed conductivity detection.

Results and Discussion

Figure 2. Example collection of VG using a Nautilus™ mini tank with a 1.6 Ω coil and a Evolv™ Mod DNA 75 color battery set to 50 W. **A)** Example chromatogram of the first puff block, consisting entirely of "wet puffs." Substantial amounts of acetic acid were produced making it difficult to discern any potential lactic acid formation. Formic acid was another major product. Minor products observed included acrylic and pyruvic acid. **B)** Chromatogram of the second puff block including dry and burnt puffs. **C)** Chromatogram of the first puff block (chromatogram "A") diluted 1:10 and overlaid with a standard (blue trace). This aided in the identification of peaks and demonstrates improved chromatography. **D)** A zoomed in section of the first puff block overlaid with a calibration standard (blue trace), showing the formation of acrylic and pyruvic acid in small amounts.

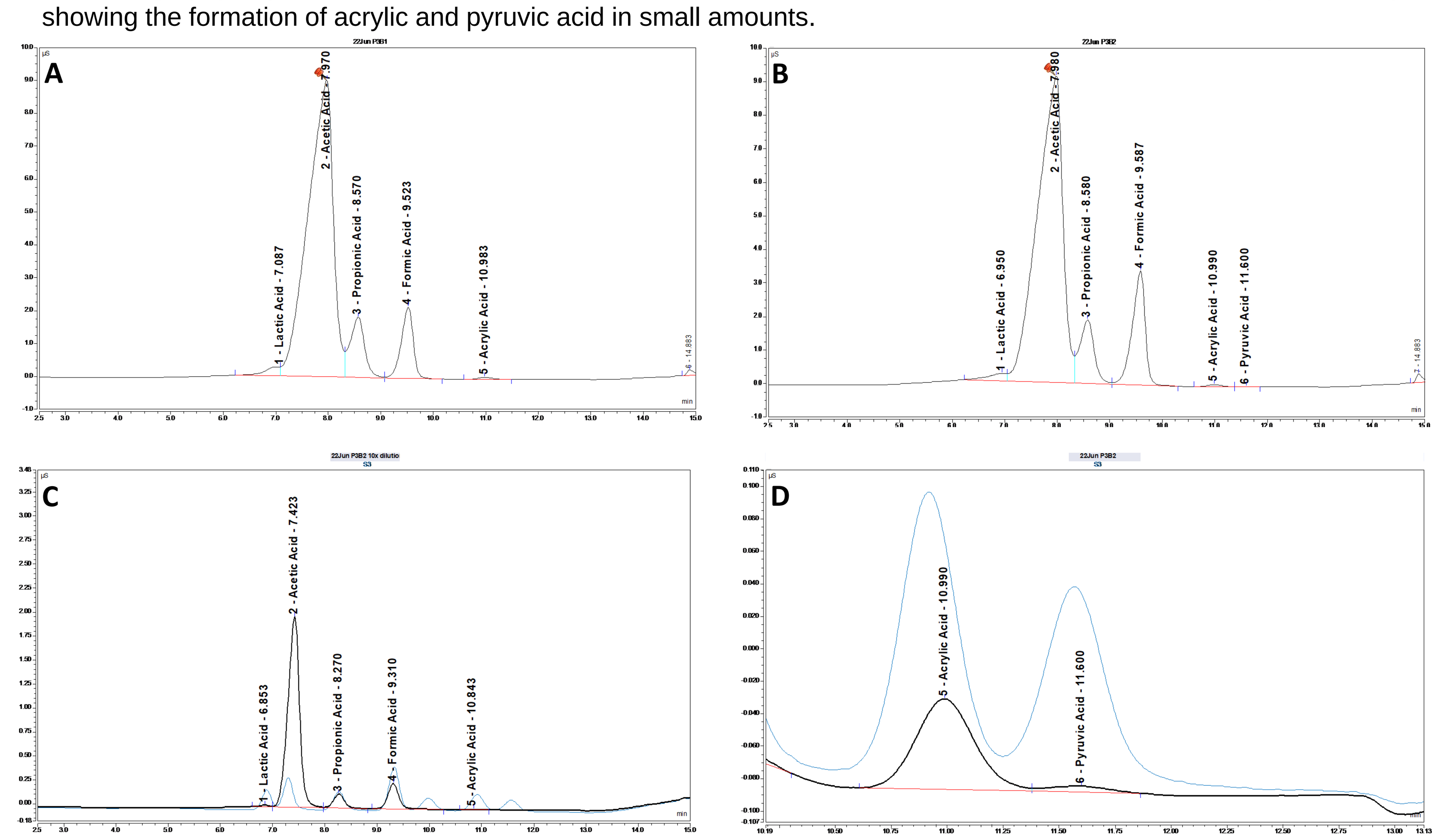
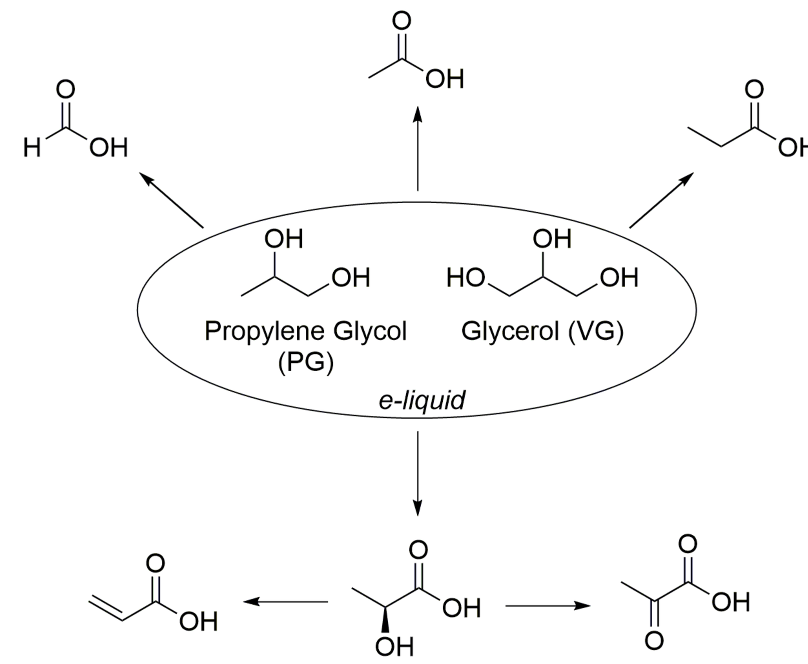


Figure 3. Example collection of PG using a Nautilus™ mini tank with a 1.6 Ω coil and a Evolv™ Mod DNA 75 color battery set to 50 W. **A)** Chromatogram of the first puff block, consisting entirely of "wet puffs." **B)** Chromatogram of the second puff block including dry and burnt puffs. Samples were collected until the coil burned out. Peaks for lactic acid, acetic acid, propionic acid, formic acid, acrylic acid and pyruvic acid were identified. **C)** Chromatogram of the second puff block (chromatogram "B") diluted 1:10 and overlaid with a standard (blue trace). This aided in the identification of peaks and demonstrates the improved chromatography. **D)** A zoomed in section of the chromatography seen in "A" overlaid with a standard demonstrating the identification of acrylic and pyruvic acid.



Scheme 1. Thermal degradation of PG and VG with proposed pathways to acrylic and pyruvic acid.

Table 1. Summary of Evolv™/Nautilus collections. (units: µg/puff)

Matrix	Watts	Lactic Acid	Acetic Acid	Propionic Acid	Formic Acid	Acrylic Acid	Pyruvic Acid
PG Block 1	12	ND	ND	ND	ND	ND	ND
	25	See Note	0.92 ± 0.226	0.08 ± 0.007	0.264 ± 0.079	0.07 ± N/A	ND
	50	2.08 ± NA	23.5 ± 34.1	3.59 ± 5.33	2.6 ± 1.95	0.177 ± 0.171	ND
PG Block 2	12	See Note	2.71 ± 0.15	0.108 ± 0.012	0.085 ± 0.013	ND	ND
	25	See Note	9.59 ± 1.81	0.593 ± 0.129	0.335 ± 0.088	0.064 ± N/A	ND
	50	1.65 ± NA	23.8 ± 26	3.36 ± 4.35	3.55 ± 2.69	0.155 ± 0.13	0.057 ± N/A
VG Block 1	12	0.043 ± 0.008	0.037 ± 0.008	ND	0.09 ± 0.009	ND	0.005 ± 0
	25	See Note	11.5 ± 0.9	0.568 ± 0.347	3.69 ± 1.25	0.138 ± 0.078	0.033 ± N/A
	50	See Note	35.8 ± 18	3.6 ± 2.88	13.8 ± 5.1	0.573 ± 0.38	0.053 ± 0.017
VG Block 2	12	0.19 ± 0.102	3.15 ± 1.71	0.05 ± 0	0.3 ± 0.1	ND	0.006 ± 0
	25	See Note	15.3 ± 6.4	0.491 ± 0.532	3.18 ± 1.81	0.083 ± 0.094	0.022 ± N/A
	50	See Note	24.5 ± 12.2	2.27 ± 1.79	8.54 ± 4.4	0.254 ± 0.206	0.061 ± 0.034

Table 2. Summary of Smok™ RPM40 collections. (units: µg/puff)

Matrix	Watts	Lactic Acid	Acetic Acid	Propionic Acid	Formic Acid	Acrylic Acid	Pyruvic Acid
PG Block 1	10	ND	ND	0.144 ± N/A	ND	ND	ND
	20	0.074 ± 0.01	0.119 ± 0.008	ND	0.096 ± 0.014	ND	ND
	40	0.067 ± 0.005	0.138 ± 0.01	0.045 ± 0	0.151 ± 0.024	ND	ND
PG Block 2	10	0.029 ± 0.001	0.04 ± 0	0.017 ± NA	0.034 ± 0.002	ND	ND
	20	See Note	1.17 ± 0.55	0.068 ± 0.03	0.083 ± 0.023	0.014 ± N/A	ND
	40	See Note	2.87 ± 0.8	0.19 ± 0.06	0.27 ± 0.144	0.024 ± 0.005	ND
VG Block 1	10	0.048 ± 0.019	0.065 ± 0.022	ND	0.085 ± 0.02	ND	ND
	20	0.064 ± 0.046	0.483 ± 0.506	0.045 ± 0.034	0.231 ± 0.164	0.026 ± N/A	ND
	40	0.062 ± 0.018	0.13 ± 0.047	ND	0.14 ± 0.034	ND	ND
VG Block 2	10	0.029 ± N/A	3.05 ± 2.24	0.104 ± 0.104	0.419 ± 0.262	0.017 ± 0.006	ND
	20	0.033 ± 0.02	1.36 ± 1.77	0.148 ± 0.146	0.217 ± 0.192	0.012 ± N/A	ND
	40	0.185 ± 0.189	1.48 ± 1.36	0.11 ± 0.01	0.22 ± 0.2	ND	ND

Note: During a number of collections, a large interfering peak was observed and eluted at the predicted lactic acid retention time, making lactic acid measurements uncertain. In this instance, dilution of samples did not improve chromatography to aid in quantification. This note serves as an indication that lactic acid may have been formed, but the exact amount is unknown.

Study Limitations/Conclusions

- For this study, only two devices were used with a single coil resistance selected for each. This was done to allow comparisons between matrix (PG vs VG) and power settings with relation to small organic acid formation. These two devices do not represent all commercially available devices with their respective tanks/coils.
- Data presented on a per puff basis. Leakage was observed during a number of collections and a per gram assessment was not always possible.
- Coil/battery performance can be variable. Decisions to make the change between puff blocks were based on visual cues and added to potential variability.
- Accurate quantification of lactic acid was difficult due to the amount of acetic acid produced during collection (see figures 2 and 3).
- Generally, small organic acid formation increased with higher device power settings.
- For both devices examined for this systematic evaluation, acetic acid and formic acid were observed in the greatest quantities (Nautilus™: up to 35 µg/puff and 13.8 µg/puff respectively; Smok™: up to 2.97 µg/puff and 0.224 µg/puff respectively).
- Acrylic acid and pyruvic acid observed with both PG and VG, with more being measured at higher power settings and more consistently with the Nautilus™/Evolv™ system (up to 0.57 and 0.6 µg/puff respectively.
- Though small organic molecules are not carcinogenic or part of the FDA's HPHC list, when devices are manufactured with large power setting options, there is an increased likelihood of acid production. This in turn could potentially impact the consumer experience.

References

1. Jablonski, J.J, Cheetham, A.G., Sill, E.D., Investigating the Potential for Ketene Generation in Flavored E-liquids via Thermal Degradation of Ester Flavorants, *Tob. Sci. Res. Conf., 2022, 75* .
2. CORESTA EVAP Sub-Group. Technical Report 2021 2019 Collaborative Study: Reference Device for e-Cigarette Aerosol Available online: https://www.coresta.org/2019-collaborative-study-reference-device-e-cigarette-aerosol-34264.html (accessed on 11Sep23).