Review of "Online measurements of cycloalkanes based on NO^+ chemical ionization in proton transfer reaction time of flight mass spectrometry (PTR-ToF-MS)" by Chen et al. (egusphere-2022-880)

General comments:

This paper describes a new technique of online measurements of cycloalkanes in the atmosphere by means of NO^+ chemical ionization mass spectrometry. The authors used major product ions of $C_nH_{2n-1}^+$ and $C_nH_{2n-3}^+$ from NO^+ chemical ionization of cyclic and bicyclic alkanes, respectively, for the measurement. After characterizing this technique in the laboratory, this technique was applied for field measurements at an urban site in southern China and a chassis dynamometer study regarding vehicle emissions. I think that this paper is generally well-written. However, I can't avoid a sense of apprehension because the authors showed the results of C10-C20 cyclic and bicyclic alkanes based on mass spectra of only five C7 and C12 cycloalkanes. The authors should show, for example, each mass spectrum of C10-C20 cycloalkanes (e. g., n-alkylcyclohexane) and discuss about interferences of other species on the ion signals of the cycloalkanes before applying the technique to the filed measurements and the chassis dynamometer study. I think that the characterizations shown in this paper are not enough. In addition, I am not sure that there is no interference on the data obtained in the filed measurements and in the chassis dynamometer study. Therefore, I recommend this paper to be revised referring to my specific comments listed below.

Specific comments:

(1) Page 5, Line 123: I would like to know ion intensities of O_2^+ and NO_2^+ relative to that of NO^+ in a flow of zero (VOC-free) -air. I guess that the O_2^+ was consumed by reactions of VOCs in a sample air. The authors should evaluate the interference of the O_2^+ reactions on the signals of cycloalkanes.

(2) Page 6, Line 125: I would like to know ion signals at 166.18 Th ($C_{12}H_{22}^+$) in Fig. S2. If there is a signal at 166.18 Th ($C_{12}H_{22}^+$), its isotopologue, $^{13}CC_{11}H_{22}^+$ (166.175 Th), can be interfered on the signals of $C_{12}H_{23}^+$ (168.18 Th). Did the authors check such the interference of isotopologues on ion signals of C10-C20 cycloalkenes obtained in the filed measurements and in the chassis dynamometer study?

(3) Page 7, Line 169−Page 8, Line 192: I would like to see each mass spectrum of C10-C20 cycloalkanes (for example, n-alkylcyclohexane) and fractions of (m-1) for the cycloalkanes, like n-alkanes in Wang et al. (2020). According to Wang et al, (2020), it was reported that the fraction was relatively small for C8-C11 n-alkanes. I wonder if octylcyclohexane (C14), for example, produce strong fragment ions, leading to the interference on smaller cycloalkanes or not.

(4) Page 8, Line 193−Page 8, Line 209: Since 2-alkenes produce $C_nH_{2n}^+$ in addition to $C_nH_{2n-1}^+$ by NO^+ ionization (Diskin et al., 2002), check ion signals of $C_nH_{2n}^+$ in the filed

measurements and in the chassis dynamometer study. If there are signals, the authors should evaluate the interference.

References:

Diskin, A. M., Wang, T. S., Smith, D., and Španěl, P.: A selected ion flow tube (SIFT), study of the reactions of H_3O^+, NO^+ and O_2^+ ions with a series of alkenes; in support of SIFT-MS, International Journal of Mass Spectrometry, 218, 87−101, 2002.

Wang, C. M., Yuan, B., Wu, C. H., Wang, S. H., Qi, J. P., Wang, B. L., Wang, Z. L., Hu, W. W., Chen, W., Ye, C. S., Wang, W. J., Sun, Y. L., Wang, C., Huang, S., Song, W., Wang, X. M., Yang, S. X., Zhang, S. Y., Xu, W. Y., Ma, N., Zhang, Z. Y., Jiang, B., Su, H., Cheng, Y. F., Wang, X. M., and Shao, M.: Measurements of higher alkanes using NO^+ chemical ionization in PTR-ToF-MS: important contributions of higher alkanes to secondary organic aerosols in China, Atmospheric Chemistry and Physics, 20, 14123−14138, 2020.