

ABSTRACT

MASTER EQUATION CALCULATIONS OF HYDROXY RADICAL PRODUCTION FROM SMALL VINOXY RADICALS

The hydroxy radical plays a central role in the formation of smog and in the fate of volatile organic compounds in the atmosphere. Whether polluted urban air or pristine rural air, its chemistry is active, day and night. Understanding the conditions by which it may be created and how it reacts is critical to accurately assessing the risk of atmospheric pollutants. A proposed source of this radical from the reaction of vinoxy radicals with oxygen is evaluated using master equation calculations. Through statistical methods, these calculations combine the reactive aspect of the chemistry with the influence of pressure to predict the kinetics and thermodynamics for the system. While unsubstituted vinoxy radicals will be a significant source of hydroxy radicals in the troposphere, our calculations predict that this potential is virtually eliminated with methyl substitution. However, when experimenting at low laboratory pressures, this additional channel will take effect.

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