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“Third-body” collision parameters for hydrocarbons, alcohols, and hydroperoxides and an effective internal rotor approach for estimating them

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Abstract

Collision rate constants and third-body collision efficiencies are calculated for more than 300 alkanes, alcohols, and hydroperoxides, for the bath gases He, Ar, H₂, and N₂, and from 300 to 2000 K. The data set includes highly branched species and species with as many as 16 nonhydrogen atoms N , and it is analyzed to develop strategies for estimating collision properties more generally. Simple analytic formulas describing the Lennard-Jones collision parameters σ and ϵ are obtained for each of the three classes of systems as a function of N . Trends in the collision efficiency range parameter $\alpha = \langle \Delta E_d \rangle$ are more complicated, and a method is developed and validated for estimating α based on the numbers and types of internal rotors and oxygen-containing groups. Specifically, the approach maps the expected value of α for a branched alkane, alcohol, or hydroperoxide onto those for the corresponding normal (linear) series via an effective number of nonhydrogen atoms N_{eff} . The prescription for N_{eff} is based on counting internal rotor types and is shown to be insensitive to temperature and fairly insensitive to the identity of the bath gas. Together, these strategies allow for the ready estimation of the collision parameters σ , ϵ , and α so long as results for the associated linear series are available.

KEYWORDS

classical trajectories, Lennard-Jones parameters, third-body collision efficiencies, unimolecular kinetics, automation

1 | INTRODUCTION

Detailed chemical kinetic models are comprised of (nowadays, often quite extensive) parameter databases describing elementary reaction rates, thermochemistry, and transport.^{1–9} The role of a priori theory as an independent source of information for populating these databases and for improving the models they reflect continues to increase.^{10–13}

Here, we consider a priori theoretical approaches for computing collision rate constants and efficiencies relevant to the prediction of transport properties^{14–16} and pressure dependence in elementary kinetics.^{17–20} These phenomena are controlled by so-called “third-body” bath gas collisions,

and we recently used trajectory-based collision parameters to compute diffusion coefficients²¹ and pressure-dependent kinetics²² with accuracies comparable to those from experiment. Our predictive work benefitted from a long history of combustion-relevant trajectory studies of collisional energy transfer (see, eg, Refs. 23–32 and the recent review from Lendvay³³) as well as quantum mechanical scattering predictions of transport properties,^{34–37} and it is similar to ongoing work from several groups (eg, Refs. 38–41).

Collisional activation is the dynamical bottleneck in the low-pressure limit of a unimolecular reaction, $A (+M) = B + C (+M)$, where the reaction rate $k_{0,M}[A][M]$ depends linearly on pressure. Chemical kinetics tabulations sometimes include