CONFIRMED ASSIGNMENTS OF ISOMERIC DIMETHYLBENZYL RADICALS GENERATED BY CORONA DISCHARGE

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Polymethylbenzyl radicals, multi-methyl-substituted benzyl radicals, have been believed to be an ideal model for understanding the torsional effect of methyl group and substitution effect on electronic transition. These radicals are mainly generated from polymethylbenzenes by electric discharge for spectroscopic observation. However, the existence of several methyl groups on the benzene ring may produce several isomeric polymethylbenzyl radicals by removing one of the C-H bonds of each methyl group at different substitution position, which makes the assignment of spectrum ambiguous. In this work, the controversial vibronic assignments of isomeric dimethylbenzyl radicals were clearly resolved by using different precursors. By using corresponding dimethylbenzyl chlorides as precursors, we identified the origins of the vibronic bands of the dimethylbenzyl radicals generated by corona discharge of precursors 1,2,3- and 1,2,4-trimethylbenzenes. From the analysis of the spectra observed from the dimethylbenzyl chlorides in a corona excited supersonic expansion using a pinhole-type glass nozzle, we revised previous assignments of the 2,6- and 2,3-dimethylbenzyl radicals as well as the 3,4-, 2,4-, and 2,5-dimethylbenzyl radicals. In addition, spectroscopic data of electronic transition and vibrational mode frequencies in the ground electronic state of each isomer were accurately determined by comparing them with those obtained by an $ab\ initio$ calculation and with the known vibrational data of precursors.