Supporting Information for *ChemPhysChem* 200400087

Formation and Decomposition of Phenylvinylperoxy Radicals in the $C_6H_5C_2H_2 + O_2$ Reaction

Y. M. Choi, J. Park, Liming Wang, and M. C. Lin

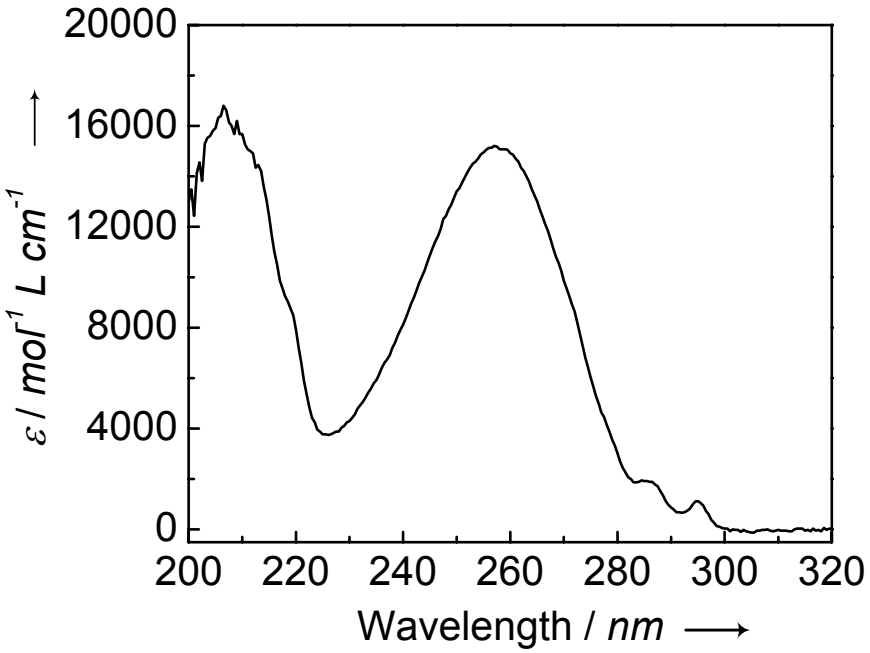

Figure S1. UV absorption spectrum of β-bromostyrene ($C_6H_5CHCHBr$) in cyclohexane solution.

Table S1. The pseudo-first order reaction rates for the $C_6H_5C_2H_2 + O_2$ association reaction and the decomposition rate of the $C_6H_5C_2H_2O_2$ at 298 K and P = 40 Torr.

$[O_2]$ (Torr)	$k_1'(s^{-1})$	$k_2'(s^{-1})$
0.020	14601	11539
0.028	14844	13046
0.030	17256	10825
0.035	17693	13767
0.039	20668	8948
0.044	19877	13690
0.046	21200	10975
0.052	21383	14900
0.054	19875	9998
0.059	21747	15091
0.063	23334	12959
0.068	26260	15155
0.072	29057	11717
0.077	28396	16442
0.080	27291	12784
0.084	31017	16385
0.088	32053	11460
0.089	29496	16602
0.096	31535	12786
0.099	30607	18164
0.105	32852	19256

Experimental

Detailed descriptions of the CRDS technique for our kinetic applications have been reported in our earlier publications.[13a] Briefly a temperature-controlled reaction cell was sealed at both the ends with highly reflective mirrors (R = 0.99995 and radius of curvature 6 m) forming the resonance cavity which can effectively increase the lifetime of a probing laser pulse with FWHM ≈ 10 ns introduced into the cavity perpendicular to both mirrors to 35 - 40 μs. The presence of absorbing species inside the cavity, however, reduces this photon decay time depending on its concentration. A KrF excimer laser (Lambda Physik, EMG102) at 248 nm of ~30 - 50 mJ was used to generate the $C_6H_5C_2H_2$ radical by the photodissociation of β-bromostyrene ($C_6H_5C_2H_2Br$). A tunable dye laser (Lambda Physik, FL 3002) of ~2 - 4 mJ pumped by a pulsed excimer laser (Lambda Physik, EMG201 MSC) at 308 nm (XeCl) was used for the detection. A small fraction of the probing photon pulse transmitted through the second mirror was directly detected by a photomultiplier tube (Hamamatsu, R955). The decay signals were sent to a digital oscilloscope (LeCroy, LS140) and then transferred to a PC for further data processing. A pulse/delay generator (SRS, DG 535) interfaced with a computer using the LabVIEW program was used to control the delay time between the photolysis and probing lasers. Typically 20 pulses were collected at the repetition rate of 2 Hz for each time delay.