J. Phys. Chem. A **2002,** *106,* 10965−10967

COMMENTS

Dissociation Channels of the 1-Propenyl Radical and Its Photolytic Precursor *cis*-1-Bromopropene[†,‡]

Johanna L. Miller,[§] Melita L. Morton,[§] Laurie J. Butler,*[,§] Fei Qi,[||] Maria J. Krisch,[§] and Jinian Shu[||]

Department of Chemistry and The James Franck Institute, University of Chicago, 5640 South Ellis Avenue, Chicago, Illinois 60637, and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

Received: September 5, 2002

The assignment of the Br atom product from the photodissociation of *cis*-1-bromopropene at 193 nm to spin−orbit excited Br($^2P_{1/2}$) given in the original paper is incorrect. The reassignment to Br($^2P_{3/2}$) alters the value reported in the original paper of the barrier energy to the lowest energy dissociation channel of the 1-propenyl radical. This Comment first describes the basis for the revised assignment: the comparison of the integrated signal at $m/e = 79$ (Br$^+$) for two photoionization energies (one of which was not presented in the original paper and so is given here in a revised Figure 7) with recent data[1] we have obtained on the Br($^2P_{1/2}$) and Br($^2P_{3/2}$) components of the Br atom signal from CH_3Br photodissociation. Then we give revised fits, substantially better than those appearing in the original paper, of the time-of-flight spectra in Figure 9, the time-of-flight of 1-propenyl radicals formed from C−Br fission that are stable to secondary dissociation. Correspondingly, we revise the component of the primary C−Br fission $P(E_T)$ in Figure 8, resulting in stable 1-propenyl radicals, derived via forward convolution from that fit. Finally, we revise the derived value of the lowest energy dissociation barrier of the 1-propenyl radical including the above changes.

The original paper correctly deduced that only one of the two low-energy spin−orbit states of the Br atom is produced by the photodissociation of *cis*-1-bromopropene at 193 nm, as the time-of-flight data at 11.5, 12.5, and 15.5 eV nominal photoionization energies had the same shape (as seen in Figure 7), but it incorrectly assigned it to the spin−orbit excited Br($^2P_{1/2}$) state. That erroneous assignment was based on the observation of good time-of-flight spectra of the Br atom product when the photoionization light source was tuned to a nominal energy of 11.5 eV, 0.3 eV lower than the literature ionization energy of 11.81 eV of Br($^2P_{3/2}$) atoms. Br($^2P_{1/2}$) atoms, having 10.54 kcal/mol more internal energy, would be expected to be ionized by 11.5 eV light, whereas Br($^2P_{3/2}$) could not be. However, the integrated signal at 11.5 eV nominal photoionization energy was only 3200 counts in 30 000 laser shots (not normalized for the average power of the photoionization light source, 26 mW, or corrected for the energy per photon), much smaller than the integrated signal obtained at 12.5 eV, 28 490 counts in 15 000 laser shots, for a similar average power (24 mW). It is possible that the Br$^+$ signal observed at the nominal 11.5 eV photoionization energy is due to Br($^2P_{3/2}$) atoms being ionized by a combination of photons in the high-energy tail or the contamination of high-energy harmonics in the photoionization source.

TABLE 1: Summary of the Time-of-Flight Spectra of $m/e = 79$ (Br$^+$), Resulting from the Photodissociation of CH_3Br at 193 nm, Taken at Two Different Photoionization Energies[a]

range of arrival times (μs)	11.5 eV spectrum integrated signal	12.5 eV spectrum integrated signal	ratio
130−136	147 ± 12	2360 ± 49	16.10 ± 1.37
137−138	361 ± 19	5636 ± 75	15.63 ± 0.85
139−140	569 ± 24	8150 ± 90	14.33 ± 0.62
141−142	610 ± 25	7016 ± 84	11.50 ± 0.49
143−145	459 ± 21	5496 ± 74	11.96 ± 0.58
146−150	157 ± 13	1711 ± 41	10.87 ± 0.91

[a] The quoted uncertainties are estimates of 1σ calculated via Poisson counting statistics. Data appearing here are corrected for neither the photoionization power nor the energy per ionizing photon.

For two reasons, it is not possible to directly evaluate the expected ratio of the integrated signals at 11.5 and 12.5 eV for either of the bromine spin−orbit states. First, the photoionization cross sections of Br($^2P_{1/2}$) as a function of energy have not been measured, and second, much of the signal is likely due to the contamination of higher harmonics passing through the gas filter, which are not well characterized. Therefore, we undertook a calibration of the relative signal levels from Br($^2P_{1/2}$) and Br($^2P_{3/2}$) at the same two photoionization energies and with the same light source bandwidth and gas filtering, using the CH_3 + Br($^2P_{1/2}$) and the CH_3 + Br($^2P_{3/2}$) photodissociation channels of CH_3Br at 193 nm as a standard. The signal from the Br atoms produced in the 193 nm photolysis of 1-bromopropene increases by a factor of 17.8 when the nominal peak of the photoionization source is tuned from 11.5 to 12.5 eV and the usual gas filtering of higher harmonics is employed, where this ratio is uncorrected for the small difference in average power and uncorrected for the significant increase in energy per photon at the two energies. (We did not include the 12.5 eV spectra in the original paper, only the 11.5 and 15.5 eV spectra, so the revised Figure 7 includes those spectra.) In comparison, the time-of-flight spectra of Br atoms from CH_3Br, crudely deconvoluted into their two overlapping components, indicate that the signal from the faster Br($^2P_{3/2}$) component increases by a factor of about 17.2 whereas the Br($^2P_{1/2}$) component increases by a factor of about 8.6 upon tuning the nominal photoionization energy from 11.5 to 12.5 eV. Thus the factor by which the Br atom signal from 1-bromopropene increases corresponds well to the factor by which the Br($^2P_{3/2}$) component of the Br atom signal from CH_3Br photodissociation increases, but not well to the factor by which the Br($^2P_{1/2}$) component increases. (The ratios given for Br atoms from CH_3Br are also not corrected for the average photoionization power, 29.1 mW at 12.5 eV, as compared to 27.2 mW at 11.5 eV, or the difference in energy per photon.) This indicates that the Br atoms from the photodissociation of 1-bromopropene at 193 nm are Br($^2P_{3/2}$), not Br($^2P_{1/2}$). (The shape of the time-of-flight spectrum would change with photoionization energy if both spin−orbit states of bromine were

---

[†] Part of the special issue "R. Stephen Berry Festschrift".

[‡] This Comment serves as an Addition and Correction to the original paper on pages 10831−10842 in this issue.

* To whom correspondence should be addressed.

[§] University of Chicago.

[||] Lawrence Berkeley National Laboratory.

10.1021/jp026919h CCC: $22.00

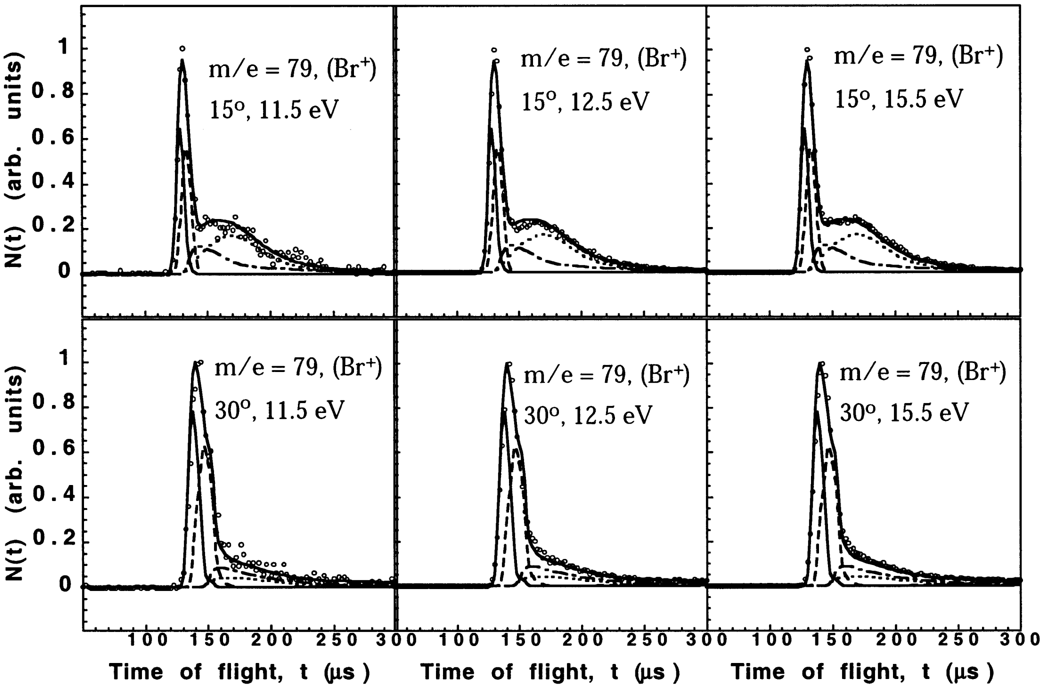

Figure 7. Time-of-flight spectra of *m/e* = 79 (Br^+), including two spectra not appearing in the original paper, taken at a nominal photoionization energy of 12.5 eV. The two 11.5 eV spectra were taken for 30 000 laser shots, and the 12.5 eV and 15.5 eV spectra were taken for 15 000 laser shots each. All six spectra are simultaneously fit by the same total C−Br fission $P(E_T)$, implying that the observed Br atoms are all produced in the same spin−orbit state. For a description of the component fits, refer to the original paper published in this issue.

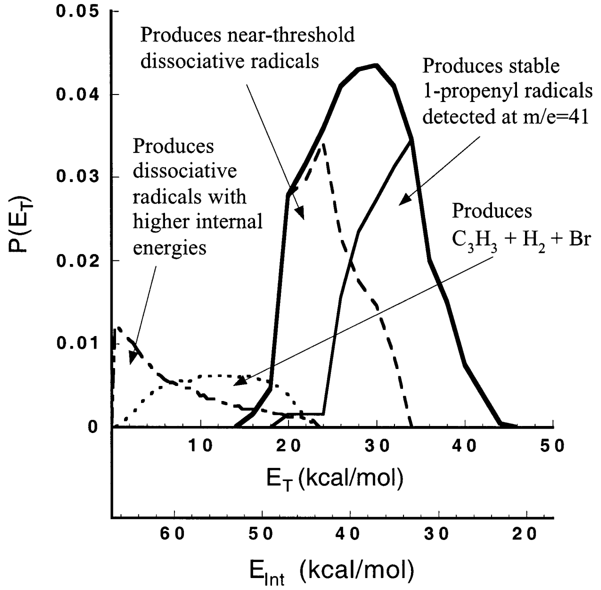

Figure 8. Revised photofragment recoil translational energy distributions, $P(E_T)$'s, obtained by forward convolution fitting of the *m/e* = 79 time-of-flight spectra. The total $P(E_T)$ is the same as the one presented in the original paper; the only revision is in the decomposition of the fast peak into components corresponding to the formation of stable and dissociative 1-propenyl radicals.

produced, so we know that only $Br(^2P_{3/2})$ is produced in the photolysis of 1-bromopropene.)

Even if one does not attempt to deconvolute the CH_3Br data into separate components, one can see a consistent decrease with arrival time in the factor by which the signal increases in tuning from 11.5 to 12.5 eV photoionization energy. Those numbers are given in Table 1. This consistent decrease in the ratio results because the $Br(^2P_{3/2})$ component dominates at the shorter arrival times whereas the $Br(^2P_{1/2})$ component dominates at the longer arrival times; so the shape of the time-of-flight spectrum changes with photoionization energy in this energy range. In fact, it is energetically impossible for $Br(^2P_{1/2})$ atoms to contribute at all to the signal observed at the fastest range of arrival times, 130−136 μs. Therefore, the factor by which the signal integrated over these channels increases is a good measure of the factor by which the signal due to $Br(^2P_{3/2})$ is expected to increase. This

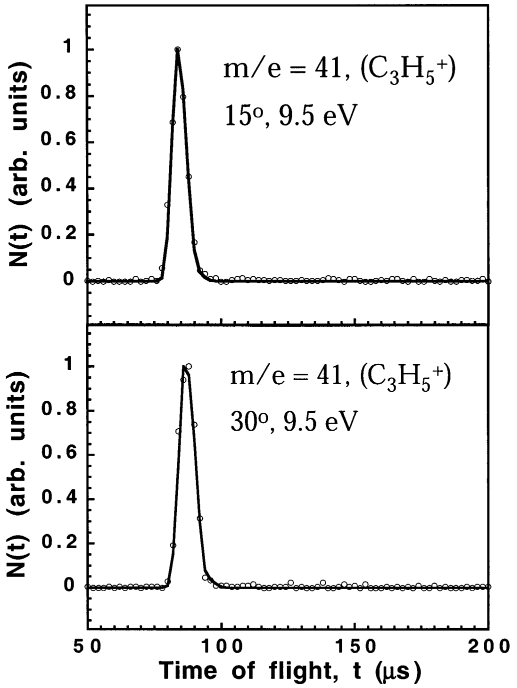

Figure 9. Revised fits of the time-of-flight spectra of *m/e* = 41 ($C_3H_5^+$) taken at source−detector angles of 15° and 30°. The 15° spectrum shown here, taken proximate to the 30° spectrum and at the same photoionization energy, replaces the spectrum shown in the original paper, taken on the subsequent day at a photoionization energy of 8.5 eV. Forward convolution fits to these spectra give the revised component of the C−Br fission $P(E_T)$ corresponding to production of stable 1-propenyl radicals.

factor, 16.10 ± 1.37, is consistent at the 95% confidence limit with the observed ratio of 17.8 for bromopropene. On the other hand, the factor by which signal integrated over the slowest channels increases is not a good measure of the factor by which signal due to Br($^2P_{1/2}$) is expected to increase. This is because Br($^2P_{3/2}$) can make a significant contribution to the signal at these long arrival times if a large amount of energy is partitioned into vibrational energy of the CH_3 fragment. However, the factor by which signal integrated over these channels increases is a good *upper bound* on the factor by which signal due to Br($^2P_{1/2}$) increases.

Two observations suggest that most of the observed signal from the photoionization of Br($^2P_{3/2}$) at the nominal energy of 11.5 eV is due to the contamination of higher energy harmonics in the photoionization source, rather than a high-energy tail in the photon distribution near 11.5 eV. First, the 10 mm × 10 mm aperture used for our data, taken at Endstation 9.0.1 of Berkeley's Advanced Light Source (ALS), gives a bandwidth of about 4.5%, but the larger spread compared to narrower slit widths is nearly exclusively on the low-energy side of the distribution; so the high-energy portion of the distribution is nearly identical to the distribution obtained with a 5 mm × 4 mm aperture, which gives a fwhm of about 2.2%.[2,3] In addition, although all prior publications from Endstation 1 report the photoioinization energy estimated from the undulator gap with a standard formula that gives an energy of 11.5 eV when the undulator gap is set to 28.7171 mm (synchrotron operated at 1.9 GeV), the *actual* energy near the peak in the photon energy distribution of the photoionization source is shifted about 0.2 eV to the red of this estimated value.[3] Thus the peak photon flux in the nominal 11.5 eV spectra is actually nearer 11.3 eV, and the photon flux drops to near zero by 11.7 eV. Thus, most of the signal from the photoionization of Br($^2P_{3/2}$) at the nominal 11.5 eV photoionization energy is likely due to a small but significant contamination from higher harmonics passing the gas filter.

With the reassignment of the Br atom signal from 1-bromopropene to Br($^2P_{3/2}$), which leaves the momentum-matched 1-propenyl radicals with 10.54 more kcal/mol of internal energy, we refit the time-of-flight spectra taken at $m/e = 41$ that appear in Figure 9 of the original paper. We had imposed the assumption in the original fits that the kinetic energy cutoff between dissociative 1-propenyl radicals and 1-propenyl radicals stable to secondary dissociation was fairly sharp (i.e., we fit the spectrum by dropping the $P(E_T)$ derived from the Br atoms TOF to zero over a 2 kcal/mol range, instead of allowing it to tail gradually to zero.) The revised fit for Figure 9 presented in this Comment allows for a more gradual onset of dissociation. That is, the $m/e = 41$ $P(E_T)$ gradually tails to zero over a range of 15 kcal/mol, so that some of the 1-propenyl radicals produced in this energy range are stable and some are dissociative. This allows for the fact that rotational energy in the nascent radical can result in a centrifugal barrier to secondary dissociation of the radical,[4,5] so a fraction of the radicals with higher internal energy than the lowest barrier energy can survive secondary dissociation. Because the C−Br fission is from an end carbon in 1-bromopropene, the recoil of the Br atoms from their 1-propenyl radical partner fragments can partition considerable rotational energy to the radical, and at a given E_T there can be a spread in the rotational energy partitioned to the radical. We show the revised fit of the $m/e = 41$ spectra in a revised Figure 9, and the revised component of the primary C−Br fission $P(E_T)$ resulting in stable 1-propenyl radicals in a revised Figure 8. (Note that the small change in this component of the $P(E_T)$ affects the neighboring component determined by subtraction, but this does not substantially alter the modeling of the C−C fission product time-of-flight spectrum in the original paper.)

Because the $P(E_T)$ used to fit the stable $m/e = 41$ 1-propenyl radicals given in this Comment is significantly superior to the fit appearing in the original paper, it is necessary to revise the derived energy barrier to the lowest energy dissociation channel of the 1-propenyl radical. The prior erroneous assignment of the Br atom spin−orbit state combined with the prior fits to the $m/e = 41$ data gave for this barrier energy

$$\begin{aligned} E_{\text{barrier to C−C fission}} &= h\nu - D_o - \\ &\quad (E_T \text{ cutoff for stable 1-propenyl}) - \Delta E(\text{Br*/Br}) \\ &= 147.9 \text{ kcal/mol} - 80.9 \text{ kcal/mol} - \\ &\quad \sim 25 \text{ kcal/mol} - 10.54 \text{ kcal/mol} \\ &= 31.5 \pm 2 \text{ kcal/mol (erroneous value)} \end{aligned}$$

This calculation was given with the reminder that when the heats of formation of the relevant species are available at 0 K, one should insert those in the above calculation to arrive at a more accurate determination and use 24 kcal/mol as the E_T cutoff, as that is more appropriate for the parent molecules with less than average internal energy (the mean internal energy of the parent molecules is about 2 kcal/mol at this nozzle temperature.)

The revised fits to the $m/e = 41$ data given above gives an E_T cutoff of 34 ± 2 kcal/mol. Note that the E_T cutoff must be determined from the energy at which the $P(E_T)$ derived from the stable 1-propenyl radicals begins to drop below the total C−Br fission $P(E_T)$ (that is, the value of the translational energy at which some, not all, of the 1-propenyl radicals begin to undergo secondary dissociation.) This accounts for the fact that a centrifugal barrier can leave a fraction of the higher internal energy 1-propenyl radicals stable to secondary dissociation. This new E_T cutoff and the correct assignment of the spin−orbit state of the Br atom product gives a revised estimate of the barrier to C−C fission in the 1-propenyl radical as follows:

$$\begin{aligned} E_{\text{barrier to C−C fission}} &= h\nu - D_o - \\ &\quad (E_T \text{ cutoff for stable 1-propenyl}) - \Delta E(\text{Br*/Br}) \\ &= 148.0 \text{ kcal/mol} - 80.9 \text{ kcal/mol} - \\ &\quad \sim 34 \text{ kcal/mol} - 0 \text{ kcal/mol} \\ &= 33 \pm 2 \text{ kcal/mol} \\ &\quad \text{(including our rough experimental uncertainty)} \end{aligned}$$

Acknowledgment. This work was supported by the National Science Foundation under Grant No. CHE-0109588. The Chemical Dynamics Beamline is supported by the Director, Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098. The ALS facility is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy, under the same contract. J.L.M. acknowledges the support of a DOD graduate fellowship, and M.J.K. acknowledges the support of an NSF graduate fellowship. We are indebted to Darcy Peterka and Musa Ahmed, who worked to better characterize the energy distribution of the photoionization source at the ALS and to correct the polynomial used to estimate the photoionization energy from a given undulator gap.

References and Notes

(1) Miller, J. L.; Krisch, M. J.; Butler, L. J.; Shu, J. Unpublished.
(2) Blank, D. A. Ph.D. Thesis, University of California Berkeley, 1997.
(3) Peterka, D. Private communication.
(4) Hintsa, E. J.; Zhao, X.; Lee, Y. T. *J. Chem. Phys.* **1990**, *92*, 2280.
(5) Szpunar, D. E.; Morton, M. L.; Butler, L. J.; Regan, P. M. *J. Phys. Chem. B* **2002**, *106*, 8086.