# ADDITIONS AND CORRECTIONS

## 2000, Volume 104A

**Martin Emrich and Peter Warneck*:** Photodissociation of Acetone in Air: Dependence on Pressure and Wavelength. Behavior of the Excited Singlet State

Page 9436. The quantum yield for the photodissociation of acetone in air is subject to a Stern−Volmer type pressure quenching, which increases with increasing wavelength in the spectral region 280−337 nm.[1,2] By combining our own data with those of Gierczak et al.,[1] we were able to show[2] that the quenching coefficient $k_M/k_D$, that is, the ratio of the rate coefficients for collisional quenching by carrier gas molecules M and dissociation of the photoexcited acetone molecule

$$\mathrm{CH_3COCH_3^* + M \rightarrow CH_3COCH_3 + M} \qquad k_M \qquad \text{(a)}$$

$$\mathrm{CH_3COCH_3^* \rightarrow CH_3 + CH_3CO} \qquad k_D \qquad \text{(b)}$$

declines exponentially with excitation energy above the dissociation threshold. In the semilogarithmic plot chosen to demonstrate this behavior, all the existing data fell reasonably well on a straight line except our point at 330 nm. The experiments had utilized the yield of peroxy acetyl nitrate (PAN)—derived from $\mathrm{CH_3CO + O_2}$ in the presence of $\mathrm{NO_2}$ as scavenger—to determine the photodissociation quantum yield. At 330 nm, in contrast to experiments at other wavelengths, the degree of $\mathrm{NO_2}$ photodissociation relative to that of acetone was undesirably high, because of the low absorption cross section of acetone. Photodissociation of $\mathrm{NO_2}$ leads to side reactions, for example, the reaction of NO with $\mathrm{CH_3O_2}$ (formed from $\mathrm{CH_3 + O_2}$), which is followed by further reactions that ultimately generate OH radicals. Therefore, the experimental data at 330 nm had required corrections to account for the additional reactions. Corrections were made by means of computer calculations based on a rather extensive reaction mechanism given in our paper. We have recently recognized that the mechanism is incomplete, in that it disregarded the reaction of acetone with $\mathrm{NO_3}$ radicals, which also are a byproduct of $\mathrm{NO_2}$ photolysis

$$\mathrm{NO_3 + CH_3COCH_3 \rightarrow HNO_3 + CH_3COCH_2} \qquad \text{(c)}$$

The rate coefficient for this reaction, $k_c = 8.5 \times 10^{-18}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, is fairly small,[3] and for this reason we had omitted the reaction. Moreover, most of the $\mathrm{NO_3}$ radicals associate with $\mathrm{NO_2}$ to form $\mathrm{N_2O_5}$, and the equilibrium set up between $\mathrm{NO_3}$ and $\mathrm{N_2O_5}$ favors the latter species. The only loss reaction included previously for $\mathrm{NO_3}$ radicals was that with NO. Owing to the rather high concentration of acetone, however, reaction c must be included in the mechanism. Consequently, it was added to the list of reactions and new calculations were made. Also included in the mechanism was the formation of acetonyl peroxy nitrate by the reaction sequence

$$\mathrm{CH_3COCH_2 + O_2 \rightarrow CH_3COCH_2OO} \qquad \text{(d)}$$

$$\mathrm{CH_3COCH_2OO + NO_2 \rightleftharpoons CH_3COCH_2OONO_2} \qquad \text{(e)}$$

where reaction d was assumed to be rapid, and for the forward and reverse pathways of reaction e the known rate coefficients $k_e = 6.4 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $k_{-e} = 10$ s$^{-1}$ were used.[4,5]

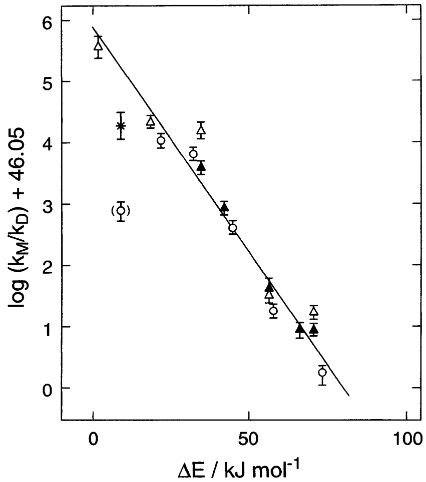

**Figure 3.**

The results of the calculations show that reaction c has indeed an effect on the dissociation quantum yield and its pressure dependence, which determines the quenching coefficient $k_M/k_D$. On the other hand, the (temporary) formation of acetonyl peroxy nitrate has no significant influence, because the comparatively long irradiation times favor decomposition. The calculations lead to the following corrected linear correlation for the inverse (corrected) quantum yield at 330 nm: $1/\Phi_{\text{diss}} = (11.2 \pm 0.7) + (1.66 \pm 0.26) \times 10^{-2}\, p$[hPa]. The value for the intercept of the straight line represented by this equation does not differ much from that derived previously (leading to a triplet quantum yield $\Phi_T = 0.\,91 \pm 0.01$ instead of $0.\,86 \pm 0.01$), but the slope is almost 4 times greater than the previous value. These data must replace the corresponding values in the last line of Table 2 of our original paper. Figure 3 in that paper, which shows the exponential decline of the quenching coefficient $k_M/k_D$ with increasing excitation energy above the dissociation threshold, must also be amended. The accompanying figure shows the corrected data point at 330 nm by an asterisk. The correction moves the point significantly closer to the straight line determined by the other data points in the figure. The 2$\sigma$ error bar indicates the uncertainty inherent in the experimental data. Systematic errors are not included. The correction is substantial, showing that the experimental method employed is no longer applicable at 300 nm (the longest wavelength explored in our study).

### References and Notes

(1) Emrich, M.; Warneck, P. *J. Phys. Chem.* **2000** *104*, 9436−9442.

(2) Gierczak, T.; Burkholder, J. B.; Bauerle, S.; Ravishankara, A. R. *Chem. Phys.* **1998**, *231*, 229−244.

(3) Wayne, R. P.; Barnes, I.; Biggs, P.; Burrows, J. P.; Canosa-Mas, C. E.; Hjorth, J.; Le Bras, G.; Moortgat, G. K.; Perner, D., Poulet, G.; Restelli, G.; Sidebottom, H. *Atmos. Environ.* **1991**, *25A*, 1−203.

(4) Sehested, J.; Christensen, L. K.; Nielsen, O. J.; Bilde, M.; Wallington, T. J.; Schneider, W. F.; Orlando, J. J.; Tyndall, G. S. *Int J. Chem. Kinet.* **1998**, *30*, 475−489.

(5) Emrich, M.; Warneck, P. *Z. Naturforsch.* **2003**, *58a*, 429−433.

10.1021/jp0407627