**Supporting Information** (No. of pages. (4))

**Oxidation of Diclofenac with Ozone in Aqueous Solution**

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\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure_S1.png}
\caption{Figure S1. Competition plot based on formaldehyde formations for the reaction of ozone with buten-3-ol and diclofenac at pH = 7, T = 20 °C}
\end{figure}

**Determination of the Rate Constant of Diclofenac with Ozone by Second-Order Kinetics**

To obtain an accurate rate constant with this technique, it has to run with one of the reactants in large excess in order to drive the reaction into (pseudo) first-order kinetics. This is not possible in this case as both O\textsubscript{3} and diclofenac absorb strongly in the same wavelength region (O\textsubscript{3}: \(\lambda_{\text{max}} = 260\) nm, \(\varepsilon = 3300\) M\textsuperscript{-1} cm\textsuperscript{-1}; diclofenac: \(\lambda_{\text{max}} = 276\) nm, \(\varepsilon = 11200\) M\textsuperscript{-1} cm\textsuperscript{-1}).
Thus, we had to choose a less accurate method, in which equimolar reactant concentrations were used to give rise second-order kinetics. Equal volumes of $6 \times 10^{-4}$ M O$_3$ and diclofenac were mixed in a stopped-flow set-up (Biologic), and the O$_3$ decay at 260 nm was followed as a function of time (Figure S2). From the data according to the second-order, a rate constant of $5.5 \times 10^5$ M$^{-1}$ s$^{-1}$ is obtained. This value is fraught with some error mainly due to some uncertainty in the actual O$_3$ concentration in the given experiment as O$_3$ continues to decay while setting up the experimental parameters in the stopped-flow experiment. As a consequence, the rate constant calculated on these data came out somewhat lower than the actual value, but comparable to the result obtained from the competition kinetics ($6.8 \times 10^5$ M$^{-1}$ s$^{-1}$).

Figure S2. Reaction of equal concentrations of diclofenac and ozone (90 µM) followed at 260 nm in a stopped-flow experiment. The solid line is a fit according to second-order kinetics.
**Figure S3.** IR, NMR and MS spectra of the main reaction product, diclofenac-2,5-iminoquinone, in the reaction of diclofenac with ozone

**Estimate of the Ozone Rate Constant with Diclofenac-2,5-iminoquinone.** Along with the degradation of diclofenac by O$_3$ in the presence of $t$-BuOH (to scavenge $^{1}$OH), its main reaction product, diclofenac-2,5-iminoquinone first builds up and then is degraded as well. Its degradation starts when 10% of the original diclofenac concentration is still present at a molar ratio of O$_3$/diclofenac = 3:1 as can be seen in Fig. 1 (A) and (B), at which 2.5 µM diclofenac and 7.5 µM iminoquinone (and other products) compete effectively for O$_3$. Actually, it is necessary to have more data to calculate the rate constant of O$_3$ with the iminoquinone from this competition. A degradation of the iminoquinone would not yet be observed at this molar ratio of O$_3$/diclofenac if the rate constant of the iminoquinone with O$_3$ were much less than 10% of the one for diclofenac. As a conservative estimate of the iminoquinone degradation potential, we took a value of 5%.