Stimuli-Responsive Materials

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Controlled Release of Encapsulated Bioactive Volatiles by Rupture of the Capsule Wall through the Light-Induced Generation of a Gas**

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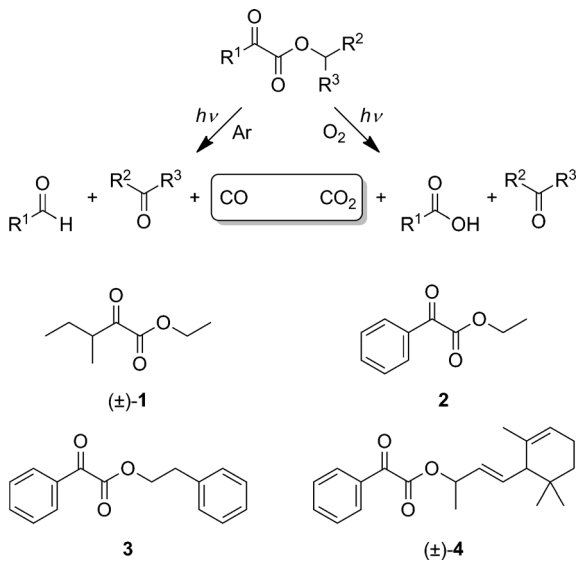
Abstract: *The encapsulation of photolabile 2-oxoacetates in core–shell microcapsules allows the light-induced, controlled release of bioactive compounds. On irradiation with UVA light these compounds degrade to generate an overpressure of gas inside the capsules, which expands or breaks the capsule wall. Headspace measurements confirmed the light-induced formation of CO and CO_2 and the successful release of the bioactive compound, while optical microscopy demonstrated the formation of gas bubbles, the cleavage of the capsule wall, and the leakage of the oil phase out of the capsule. The efficiency of the delivery system depends on the structure of the 2-oxoacetate, the quantity used with respect to the thickness of the capsule wall, and the intensity of the irradiating UVA light.*

Ambient daylight is one of the most important natural energy sources to enable and control fundamental biological processes.[1] UV light is a convenient and relatively mild "reagent" for the formation, cleavage, and isomerization of covalent bonds.[2] In particular, its orthogonality to other reaction conditions makes it an interesting trigger for the design of photo-responsive delivery systems with potential applications in biology and medicine.[3–7] Biologically active molecules can either be released from suitably designed conjugates by light-induced cleavage of a covalent bond,[3,4] or be delivered from light-sensitive carrier systems, such as self-assembled nanostructures[5] and polymer-based core–shell capsules[6,7] into which the bioactive compounds have previously been physically trapped. Traditional core–shell capsules that release biomolecules on exposure to UV light[7] include those based on the photochemical decomposition of a capsule wall containing photocleavable moieties,[8] on a structural change in the wall owing to the presence of photoisomerizable units,[9] on the incorporation of TiO_2 nanoparticles into the capsule structure,[10] or on the generation of reactive oxygen species by photosensitization using porphyrin units located in the capsule shell.[11] In all cases, the photoresponsive units need to be specifically built into the capsule shell, which is not always easy to achieve.

Hu and Neckers[12] and we[13] previously studied 2-oxoacetates (α-ketoesters) as precursors (profragrances) for the light-induced controlled release of fragrance aldehydes and ketones. On photoirradiation at around 360 nm, they fragment according to the Norrish type II mechanism.[14] The reaction, originally reported 80 years ago by Bamford and Norrish for the photochemical degradation of carbonyl compounds,[15] tolerates a broad structural variety and was shown to efficiently release volatile aldehydes, ketones, esters, lactones, or olefins.[4,16] Nevertheless, 2-oxoacetates represent a special class of compounds because they form the desired aldehyde and ketone together with a molar equivalent of a gas. Depending on whether the reaction is performed in the absence or presence of oxygen, CO or CO_2 is obtained (Scheme 1).[14] We wondered whether the daylight-induced formation of CO and/or CO_2 from 2-oxoacetates if they were encapsulated inside core–shell microcapsules could be used to



Scheme 1. Norrish type II photofragmentation of 2-oxoacetates with the formation of CO in the absence of oxygen and of CO_2 in the presence of oxygen[14] and structures of alkyl (**1**) and aryl 2-oxoacetates (**2**–**4**) of primary (**1**–**3**) and secondary alcohols (**4**) used in the present work.

generate an overpressure inside the capsule that would expand or break the shell of the capsules and thus allow the release of bioactive compounds in practical applications.[17] More than 30 years ago, Mathiowitz et al. reported the UV light-induced formation of N_2 from encapsulated 2,2′-azobis(2-methylpropionitrile) (AIBN) to break the capsule wall.[18] They monitored the release of N_2 from the capsules

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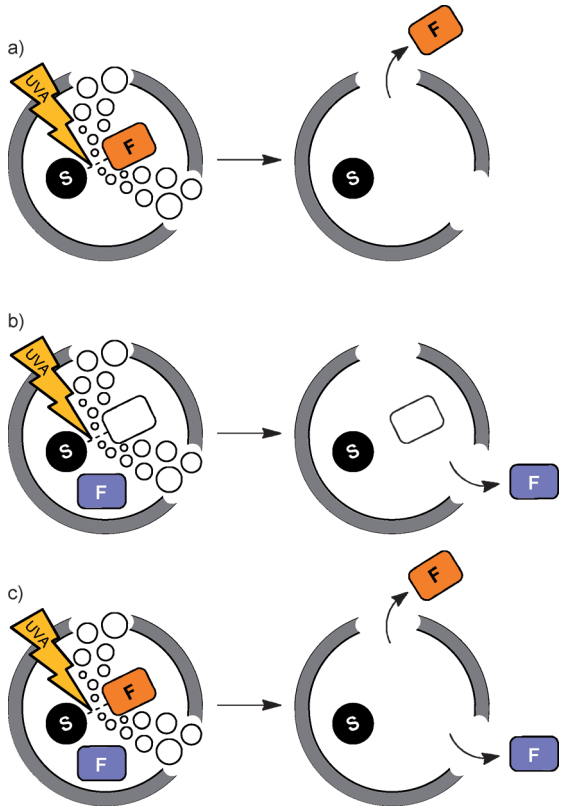
and suggested that their system could deliver co-encapsulated bioactive molecules. However, the successful release of active compounds has not been demonstrated. To our surprise, this concept has not been investigated in much further detail since then.

Using fragrances as volatile, low-molecular weight bioactive molecules, several delivery strategies can be adopted for their light-induced release from microcapsules (Scheme 2).



Scheme 2. Strategies to release fragrances (or other bioactive compounds) by UVA-induced formation of a gas from encapsulated photolabile precursors (e.g. 2-oxoacetates). a) Light-induced generation of the gas and simultaneous formation of a fragrance (F, orange) covalently attached to a photo-responsive substrate (S). b) Light-induced generation of the gas and release of a non-covalently attached fragrance (F, violet). c) Light-induced generation of the gas and release of a fragrance (F, orange) covalently attached to a substrate (S) together with another non-covalently attached fragrance (F, violet).

Encapsulation of 2-oxoacetate profragrances[13] would allow the simultaneous generation of a gas to expand or break the capsule shell together with a fragrance aldehyde or ketone (Scheme 2a). If the photolabile 2-oxoacetate is only used to generate an overpressure by forming the gas and an odorless carbonyl compound (or a carbonyl compound without particular interest for perfumery), then the co-encapsulation of other non-covalently linked fragrances should allow the release of these compounds (Scheme 2b). Finally, in the case of encapsulating a photolabile 2-oxoacetate profragrance with other fragrance molecules, several different types of fragrances should be delivered at the same time (Scheme 2c).

Because polymers are permeable to gases, it is necessary to generate a sufficient overpressure inside the microcapsules to expand or break the capsule wall and thus to release the fragrances. As a consequence, the degradation of the 2-oxoacetates needs to be much faster than the diffusion of the generated gas across the capsule wall.

To establish the guidelines for the selection of suitable 2-oxoacetates as gas precursors, we investigated their rates of degradation on exposure to UVA light in solution. The structures of the oxoacetates were selected to cover alkyl (**1**) and aryl derivatives (**2**–**4**) of primary (**1**–**3**) and secondary alcohols (**4**, Scheme 1). Whereas structures **1** and **2** release acetaldehyde, which in the present case is not of interest for perfumery applications, derivatives **3** and **4** release the fragrances 2-phenylacetaldehyde and (*E*)-4-(2,6,6-trimethylcyclohex-2-en-1-yl)but-3-en-2-one (α-ionone), respectively. To evaluate the influence of the precursor structures on their rate of degradation with all other parameters being constant, we performed kinetic measurements in a not-degassed solution under realistic everyday conditions. 2-Oxoacetates **1**–**4** in acetonitrile (8 mM) were thus irradiated with a UVA lamp at 3.1 mW cm^{-2} for a total time of 2 h.[19] The degradation of the compounds followed first-order kinetics as determined by gas chromatography (GC) and/or by high-performance liquid chromatography (HPLC). Observed first-order rate constants (k_{obs}) and half-life times ($t_{1/2}$) for the photolysis of oxoacetates **1**–**4** are listed in Table 1.

Table 1: Light-induced degradation of 2-oxoacetates **1**–**4**.[a]

2-Oxoacetate	Method	k_{obs} [s^{-1}]	$t_{1/2}$ [min]
(±)-**1**	GC	3.10×10^{-4}	37.3
2	GC	7.09×10^{-4}	16.3
	HPLC	7.87×10^{-4}	14.7
3	HPLC	6.84×10^{-4}	16.9
(±)-**4**	HPLC	4.17×10^{-4}	27.7

[a] Observed first-order rate constants (k_{obs}) and half-life times ($t_{1/2}$) for the light-induced degradation of 2-oxoacetates **1**–**4** (at 8 mM) in acetonitrile (not degassed) on exposure to UVA light of 3.1 mW cm^{-2} for 2 h.

The data show that 2-oxoacetates **1**–**4** all degrade in a well-defined manner at rates of the same order of magnitude. Aryl 2-oxoacetates (**2**–**4**) reacted faster than their alkyl analogue (**1**), and the release of aldehydes (**2** and **3**) was found to be slightly more efficient than that of ketones (**4**, Table 1). With half-life times of about 15–40 min under real-life UVA irradiation conditions, we estimated that the light-induced degradation of 2-oxoacetates **1**–**4** might be sufficiently fast to build up an overpressure inside a suitably designed core–shell microcapsule.

For the encapsulation and photorelease studies, we used polyurea core–shell microcapsules,[20] which are obtained from an oil-in-water emulsion by interfacial polyaddition of diamines and polyisocyanates.[21] The release of encapsulated fragrances usually occurs by mechanical rupture of the shell by rubbing of the capsules in application.[20] Polyurea microcapsules were prepared according to literature procedures[20] by polyaddition of Takenate D-110N as the polyisocyanate

and 1*H*-1,2,4-triazole-3,5-diamine (guanazole) as the diamine at a fixed molar ratio of isocyanate/amine groups of 0.7. Glassy, oil-insoluble polyurea capsules with an average diameter varying between 10 to 25 μm and a glass-transition temperature (T_g) of 81 °C, well above room temperature, were obtained.

For a first proof of concept, we encapsulated pure 2-oxoacetate **3** according to the strategy depicted in Scheme 2a. From an emulsion of **3** at 25 wt% in water, stabilized with poly(vinyl alcohol), a dispersion of microcapsules **A** with a shell/core ratio of 0.19 was obtained.

The capsule dispersion was diluted to contain a constant total amount of fragrance to be released. A small aliquot of this dispersion was then pipetted onto a glass slide and left drying in the dark for 1 day. The amount of fragrance released from the sample was quantified by dynamic headspace analysis.[22] A first headspace concentration was determined after equilibrating the sample for 15 min in the dark. The sample was then irradiated with UVA light at 3.1 mW cm^{-2} for a total time of 2 h,[19] and further headspace concentrations were measured at constant time intervals.

Figure 1a shows the amount of 2-phenylacetaldehyde released from precursor **3** encapsulated in microcapsules **A** in comparison to an equimolar amount of film of non-encapsulated **3** as the reference.

The headspace data indicated that almost no volatiles were detected at the beginning of the measurements when the sample was kept in the dark. After the UVA lamp was switched on, a spontaneous release of the fragrance aldehyde was observed in both cases. Although slightly lower amounts of aldehyde were released from encapsulated **3** than from the non-encapsulated precursor film, the shapes of the two curves were similar. The synchronized response of encapsulated and non-encapsulated profragrance **3** to the light trigger demonstrated that the presence of the capsule had almost no impact on the release of the aldehyde into the headspace.

Repeating the irradiation of microcapsules **A** by replacing the Tenax cartridges from the headspace sampling with an in-series connection of a CO and a CO_2 gas detector showed that the amount of CO and CO_2 in the air increased by about 10 ppm immediately after the UVA lamp was switched on (Figure 1a). Both gases are thus generated on photoirradiation of the encapsulated profragrance **3**. The fact that the formation of the gas and the release of the fragrance aldehyde into the headspace occurred simultaneously indicated an instantaneous expansion or rupture of the capsule wall.

We investigated if it was possible to release other fragrance molecules from the microcapsules when they are encapsulated together with a photolabile 2-oxoacetate (as outlined in Scheme 2b). Microcapsules **B** were prepared by replacing profragrance **3** with a 1:1 mixture of alkyl 2-oxoacetate **1** and (±)-methyl 2,2-dimethyl-6-methylenecyclohexanecarboxylate (Romascone, Figure 1b)[23] as a pure model fragrance compound to be released, while microcapsules **C** were loaded with a 1:1 mixture of aryl 2-oxoacetate **2** and Romascone. Finally, we prepared a reference capsule without oxoacetate (microcapsule **D**), which consisted of a 1:1 mixture of Romascone and (±)-methyl 2-(3-oxo-2-pentylcyclopentyl)acetate (Hedione) as the model

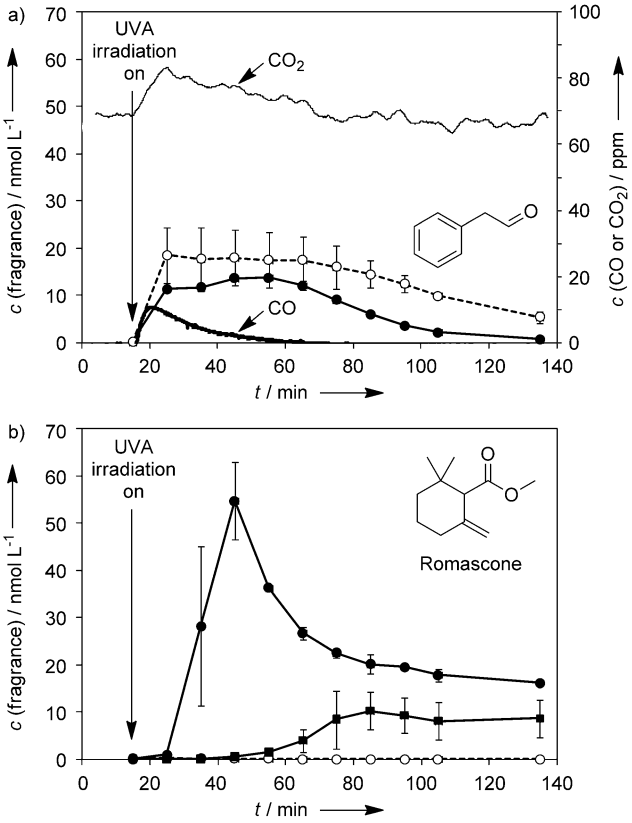


Figure 1. Dynamic headspace analysis for the light-induced release of fragrances from 2-oxoacetate-containing polyurea core–shell microcapsules. a) Release of 2-phenylacetaldehyde from encapsulated 2-oxoacetate **3** (microcapsule **A**, ●), and from a film of non-encapsulated **3** (○, reference) and formation of CO (▬) and CO_2 (——, smoothed) on irradiation of microcapsule **A**. b) Release of Romascone encapsulated together with 2-oxoacetate **1** (microcapsule **B**, ■) or **2** (microcapsule **C**, ●) or with Hedione (microcapsule **D**, ○, reference), each at 50 wt%. All data are average values of at least two measurements.

fragrances. Photoirradiation and monitoring the evaporation of Romascone by dynamic headspace analyses as described above afforded the data illustrated in Figure 1b.

As expected, the reference microcapsule **D** released almost no fragrance during the entire measurement. Although the amount of oxoacetate was lower than in **A**, microcapsules **C** released the encapsulated Romascone efficiently after short exposure to UVA light. A maximum of the model fragrance was detected in the headspace after 30 min of irradiation (45 min after the start of the measurement). In contrast to microcapsules **C**, the release of the fragrance from microcapsules **B** was found to be considerably slower and less intense. This difference can be correlated to the rates of decomposition of the two 2-oxoacetates and thus the speed of the formation of the gas. As shown earlier (Table 1), aryl oxoacetate **2** degraded about twice as fast as its alkyl analogue **1** and could therefore more efficiently generate the required overpressure inside the capsule to expand or burst the capsule wall.

In addition to its structure, the amount of 2-oxoacetate encapsulated in the microcapsules was expected to influence

the efficiency of the delivery system. We thus prepared microcapsules containing different quantities of photolabile 2-oxoacetate **2** and topped the amount up to 100 wt% with Romascone. Besides microcapsule **C** (containing 50 wt% of **2**), we investigated microcapsules **E** (with 80 wt% of **2**) and **F** (using 25 wt% of **2**). The quantity of capsules irradiated was adjusted to release the same total amount of fragrance in all cases. Figure 2a indicates the average headspace concentrations of Romascone measured at the peak maxima after 10–30 min of UVA irradiation as a function of the amount of 2-oxoacetate **2** encapsulated.

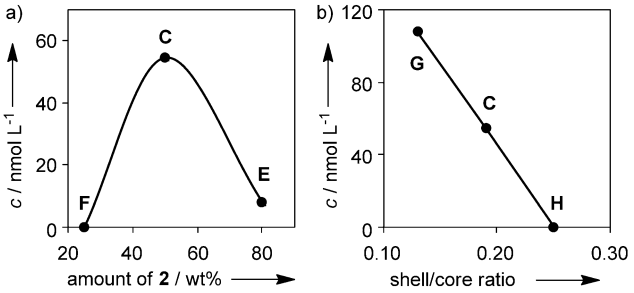


Figure 2. Dynamic headspace concentrations of Romascone a) released from microcapsules **C**, **E**, and **F** as a function of the amount of encapsulated 2-oxoacetate **2** and b) as a function of the shell/core ratio of microcapsules **C**, **G**, and **H**. The reported headspace concentrations correspond to the peak maxima observed after 10–30 min of photoirradiation.

As almost no fragrance was released from microcapsules **F**, 25 wt% of oxoacetate **2** seemed to be insufficient to release the fragrance under the given conditions. The highest amount of Romascone was released from microcapsule **C** with 50 wt% of **2**, while microcapsule **E**, containing 80 wt% of **2**, released much less fragrance. This result seems surprising at first; it might, however, be explained by the fact that the composition of the oil phase influences the droplet size of the emulsion and thus the average size of the microcapsules. With an average diameter of 22.6 μm, capsule **E** is almost twice as big as capsule **C** (11.6 μm) and thus has a considerably thicker capsule wall, which is more difficult to rupture.

The thickness of the wall with respect to the size of the capsules,[24] has an important impact on the overall efficiency of the delivery system. Microcapsules **A**–**F** were all prepared with a constant shell/core ratio of 0.19. We thus decided to vary the shell thickness and prepared two more microcapsules with the same core composition as that of microcapsule **C**, but with shell/core ratios of 0.13 (microcapsule **G**, thinner shell) and 0.25 (microcapsule **H**, thicker shell). The peak maxima of the Romascone headspace concentrations measured after 10–30 min of UVA irradiation showed that microcapsules **G** were the most efficient capsules tested (Figure 2b), and that the amount of Romascone released into the headspace decreased with an increasing shell/core ratio, if all other parameters were left constant.

Finally, the intensity of the irradiating light influences the rate of degradation of the oxoacetates[4] and is thus another important parameter to impact the efficiency of fragrance release from the microcapsules. Figure 3 shows a series of optical microscopy images that were recorded during the irradiation of microcapsules **E**, which were exposed to the UVA light of the microscope. Figure 3a shows the capsules before irradiation, and the other images were taken at intervals of 5 s after switching on the lamp (see also the video in the Supporting Information). After 15–20 s of exposure to the light, a gas bubble forms inside some of the capsules (black arrows in Figure 3d,e). Figure 3e even shows the spontaneous rupture of the shell in one of the capsules followed by the leakage of the oil phase out of the capsule (white arrows). The almost instantaneous release of the fragrance under the microscope is a consequence of the light of the microscope being much more focused and thus more intense than the diffuse UVA light emitted from the lamp used in the previous experiments.

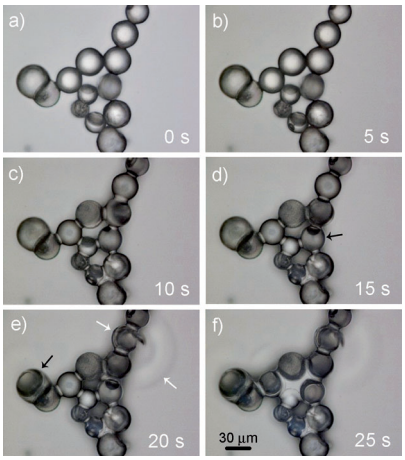


Figure 3. Optical microscopy images for the photoirradiation of microcapsules **E** containing 80 wt% of photolabile 2-oxoacetate **2** and 20 wt% of Romascone as the fragrance to be released. Image a) was taken before irradiation, images b) to f) at 5 s intervals after switching on the UVA light source. The black arrows in d) and e) show the formation of gas bubbles inside two of the capsules. The white arrows in (e) demonstrate the cleavage of a capsule's shell and the leakage of the oil phase out of the capsule. The video from which these images have been taken is part of the Supporting Information.

The encapsulation of photolabile 2-oxoacetates into suitably designed polyurea core–shell microcapsules is a simple, inexpensive, and highly efficient way to control the light-induced release of bioactive compounds. On exposure to natural daylight, encapsulated 2-oxoacetates degrade to form CO and CO_2 at rates that are sufficient to generate an overpressure of gas to expand or break the capsule wall and thus liberate the entrapped compounds. Headspace analysis demonstrated both the simultaneous formation of the gas to cleave the capsule and the release of an encapsulated bioactive compound as a direct consequence of UVA irradiation. The formation of gas bubbles inside the capsules, the cleavage of the capsule wall and the leakage of the oil phase could be followed by optical microscopy.

Our strategy could probably be applied to a broad variety of structures other than the 2-oxoacetates reported in this work, if they are able to generate a gas on exposure to light. Our approach is generally applicable to different types of

capsules, and is particularly suitable for the encapsulation and controlled release of highly volatile, low-molecular weight bioactive compounds, such as fragrances, but also for the release of semiochemicals used in the communication between species, or for the delivery of agrochemicals. Because of the simplicity of the present concept, we are convinced that it will be a valuable alternative to the current light-responsive delivery systems, which typically rely on the use of polymers containing photocleavable or photoisomerizable units, and that our work could be adapted to control the light-induced release of bioactive compounds in other areas of life-sciences.

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Communications

Stimuli-Responsive Materials

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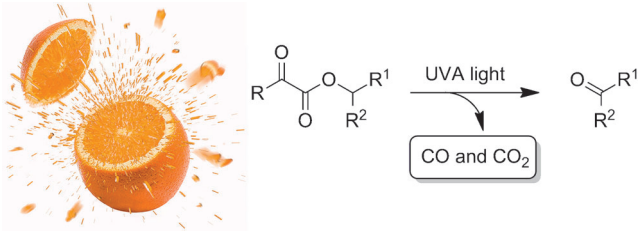
Controlled Release of Encapsulated Bioactive Volatiles by Rupture of the Capsule Wall through the Light-Induced Generation of a Gas



A burst of aroma: Bioactive compounds, such as fragrances, can be efficiently released from core–shell microcapsules by the light-induced decomposition of encapsulated 2-oxoacetates, generating an overpressure of gas that expands or even breaks the capsule wall.