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Thermal Stability of Peroxy Acyl Nitrates Formed in the Oxidation of $C_xF_{2x+1}CH_2C(O)H$ (x = 1,6) in the Presence of NO_2

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ABSTRACT: The formation of $C_xF_{2x+1}CH_2C(O)OONO_2$ (x = 1,6) from the photooxidation of $C_xF_{2x+1}CH_2C(O)H$ (x = 1,6) in the presence of NO_2 was investigated. The infrared spectrum of $C_6F_{13}CH_2C(O)OONO_2$ is reported for the first time, and thermal stability for both peroxynitrates at 295 K and 9.0 mbar is informed. Kinetic parameters (activation energy and pre-exponential factor) for $CF_3CH_2C(O)OONO_2$ at 9.0 and 1000 mbar are: 108 ± 2 kJ/mol, 1.5×10^{15} and 114 ± 2 kJ/mol, 2.4×10^{16}, respectively. A comparison is made between fluoro and hydrogenated peroxy acyl nitrates.
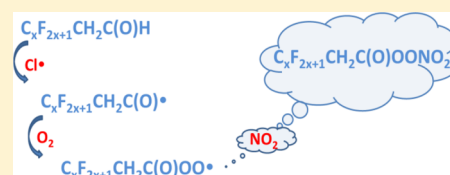
INTRODUCTION

The oxidation of telomeric alcohols (FTOHs), which have a wide variety of industrial applications, leads to the formation of fluorinated telomeric aldehydes (FTAHs, $C_xF_{2x+1}CH_2C(O)H$) and perfluorocarboxylics acids[1] (PFCAs, $C_nF_{2n+1}C(O)OH$), which are highly persistent in the environment and have been found to be present in fauna from the Great Lakes[2] up to the Arctic.[3] In particular, $C_6F_{13}CH_2C(O)H$ (FTAL 6:2) is formed from the degradation of FTOH 6:2,[4] whereas $CF_3CH_2C(O)H$ has been reported as the primary oxidation product of $CF_3CH_2CH_2OH$.[5]

The UV absorption cross sections and the photochemistry of FTAL 6:2 were studied[6] as well as its reaction with both chlorine atoms,[4,7,8] for which the authors measured a rate constant of $(2.1 \pm 0.5) \times 10^{-12}$, $(2.8 \pm 0.7) \times 10^{-12}$, and $(1.8 \pm 0.2) \times 10^{-11}$ cm³ molec⁻¹ s⁻¹, respectively, and OH radicals,[4] with a reported coefficient of $(2.2 \pm 0.3) \times 10^{-12}$ cm³ molec⁻¹ s⁻¹. Its oxidation in the absence of NO_x gives n-$C_6F_{13}C(O)H$, CF_2O, CO_2, and CO as the only products. Chiappero et al.[4] concluded that most of the reaction between $C_nF_{2n+1}CH_2C(O)H$ and chlorine atoms occurs via abstraction of the aldehyde hydrogen atom, not being substantially modified by the length of the fluorinated C_nF_{2n+1} group.

Kelly et al.[5] have measured the quantum yield of the photolysis of $CF_3CH_2C(O)H$, $\phi < 0.04$ and its rate constant with OH radicals $(2.96 \pm 0.04) \times 10^{-12}$ cm³ molec⁻¹ s⁻¹ and chlorine atoms $(25.7 \pm 0.4) \times 10^{-12}$ cm³ molec⁻¹ s⁻¹. Its oxidation in the absence of NO leads to the formation of $CF_3C(O)H$, $CF_3CH_2C(O)OH$, and $CF_3CH_2C(O)OOH$.[5] When NOx is present, CF_2O and $CF_3CH_2C(O)OONO_2$ are additionally formed.[5,9]

As it is well known, peroxyacyl nitrates ($RC(O)OONO_2$) are formed in situ by photochemical reactions involving volatile organic compounds (aldehydes, hydrocarbons, ketones, etc.) and nitrogen oxides, and they are also important reservoir species due to their stability. Among them, peroxyacetyl ($CH_3C(O)OONO_2$, PAN), peroxypropionyl ($CH_3CH_2C(O)OONO_2$, PPN), peroxyisobutyryl (PiBN, $((CH_3)_2CHC(O)OONO_2)$, peroxybutyryl (PnBN, $CH_3(CH_2)_2C(O)OONO_2$), and peroxybenzoyl ($C_6H_5C(O)OONO_2$, PBzN) nitrates have been detected in the atmosphere.[10−14] To provide information about the thermal stability of the peroxynitrates formed by the oxidation of FTAL 6:2 and $CF_3CH_2C(O)H$ in the presence of NO_2, we prepared both and measured their decomposition rate constants as a function of temperature and total pressure.

EXPERIMENTAL SECTION

Reagents. Samples of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanal and 3,3,3-trifluoropropionaldehyde (TFPA, $CF_3CH_2C(O)H$) were used as provided without any special purification. Oxygen (5.0), nitrogen (5.0), and nitrogen monoxide (5.1) were provided by AGA. Cl_2 (>99%) was prepared by dehydration of HCl, and NO_2 (>99%) was obtained from thermal decomposition of $Pb(NO_3)_2$.

Procedure. Gas samples were manipulated in a glass vacuum line equipped with two capacitance pressure gauges. All photolyses were carried out in a 5 L glass flask, using black lamps ($\lambda > 330$ nm) to initiate the oxidation from chlorine atoms.

Synthesis and Characterization. $C_6F_{13}CH_2C(O)OONO_2$. Photolyses of mixtures containing $C_6F_{13}CH_2C(O)H$ (0.6 mbar), Cl_2 (0.9 mbar), NO_2 (0.9 mbar), and O_2 (1000 mbar) were performed at 295 K. Their progress was monitored at 0, 30, 50, and 75 min by transferring portions of the mixtures to a long path infrared gas cell (optical path: 9 m) and recording infrared spectra. It was stopped before the NO_2 was

completely consumed to shift the equilibrium ROONO$_2$ ⇆ ROO$^{\bullet}$ + NO$_2$ to the peroxynitrate formation (see below).

After infrared analysis, the resulting mixture was collected by passing it through traps at liquid nitrogen temperature to remove oxygen excess. Subsequent distillation at 193 K allowed elimination of carbonyl fluoride (CF$_2$O), ClNO, and carbon dioxide formed as photooxidation products. The remains were kept with other different batches for further purification. They contained peroxynitrate, C$_6$F$_{13}$CH$_2$ONO$_2$, and C$_6$F$_{13}$CH$_2$C-(O)H, three substances which are difficult to separate from each other by trap-to-trap distillation under vacuum. Therefore, to obtain the infrared spectra of C$_6$F$_{13}$CH$_2$ONO$_2$ and C$_6$F$_{13}$CH$_2$C(O)OONO$_2$, we distilled in our three U-trap system (233, 213, and 77 K) the mixture as much as possible until every U-trap contained mostly one of each component. From successive subtraction the spectra of both nitrate and peroxynitrate were obtained. The content of the U-trap containing mainly the peroxynitrate was transferred to the infrared cell, and NO was added to study its thermal stability.

CF$_3$CH$_2$C(O)OONO$_2$. Mixtures of CF$_3$CH$_2$C(O)H (4.0 mbar), Cl$_2$ (3.1 mbar), NO$_2$ (3.5 mbar), and O$_2$ (1000 mbar) were photolyzed and then distilled, as previously described for C$_6$F$_{13}$CH$_2$C(O)OONO$_2$. This procedure permitted the possibility of getting good quantities of this peroxynitrate, with purity above 95% according to the IR bands analyzed. Other authors have seen the IR peaks but have not prepared bulk quantities.[4] The infrared spectrum of CF$_3$CH$_2$C(O)OONO$_2$ (bands at 793, 1056, 1205, 1243, 1304, 1761, 1851 cm^{-1}) is in good agreement with all of the bands reported by Hurley et al. 2005,[9] the first research group to report such information.

Thermal stability was determined by the addition of NO, in the temperature range between 288 and 307 K, at 9.0 and 1000 mbar of total pressure. At 307 K, pressure dependence of the rate constant was analyzed between 3.3 and 1000 mbar.

RESULTS AND DISCUSSION

Photooxidation Mechanism of C$_6$F$_{13}$CH$_2$C(O)H in the Presence of NO$_2$. Figure 1 depicts the infrared spectra obtained in the photooxidation of C$_6$F$_{13}$CH$_2$C(O)H before and 30 min after irradiation and their subtraction showing the resulting products. Observation of the whole infrared spectrum of the products (middle trace in Figure) reveals the formation
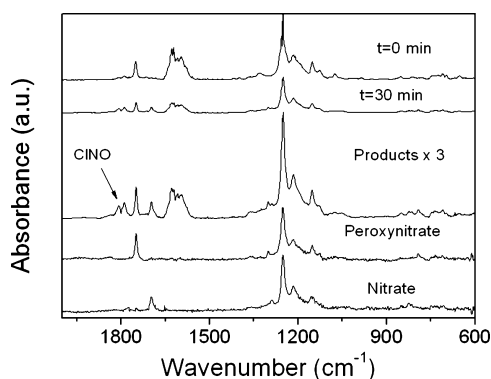
of ClNO (around 1800 cm^{-1}) and CO$_2$ (667 cm^{-1}) and the appearance of peaks at 795, 1749 and 825, 1694 cm^{-1} corresponding to C$_6$F$_{13}$CH$_2$C(O)OONO$_2$ and C$_6$F$_{13}$CH$_2$ONO$_2$, respectively. Not even at 30 min was CF$_2$O detected as a product, which is in accordance with the high NO$_2$ concentrations still present in the system (see below). Infrared spectra of peroxynitrate and nitrate were included for comparison.

Table 1 lists the main peaks of the products identified in this work together with those corresponding to hydrogenated and
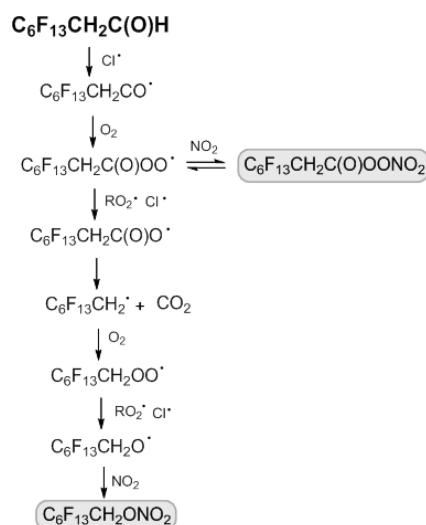
Table 1. Comparison of Selected Wavenumbers for Similar Peroxynitrates (RC(O)OONO$_2$) and Nitrates (RONO$_2$)

| R	wavenumber (cm^{-1})		
peroxynitrate	$\nu_{as}(NO_2)$	$\delta_s(NO_2)$	reference
CH$_3$	1741	794	15
CF$_3$CH$_2$	1750	794	9
C$_4$F$_9$CH$_2$	1749	791	16
C$_6$F$_{13}$CH$_2$	*1749*	*795*	*this work*
CF$_3$	1761	793	17
nitrate	$\nu_{as}(NO_2)$	$\delta_s(NO_2)$	
CH$_3$	1672	854	18
CF$_3$CH$_2$	1694	826	19
C$_4$F$_9$CH$_2$	1695		16
C$_6$F$_{13}$CH$_2$	*1694*	*825*	*this work*
CF$_3$	1748	788	20

fluorinated peroxynitrates as well as nitrates of similar structures. As it can be seen, there is a clear-cut difference in the wavenumbers for a fully hydrogenated peroxynitrate and a fully fluorinated one, being the IR bands of the mixed peroxynitrates always located between them. Note that the band absorptions for $\nu_{as}(NO_2)$ and $\delta_s(NO_2)$ are similar for both CF$_3$CH$_2$C(O)OONO$_2$ and C$_6$F$_{13}$CH$_2$C(O)OONO$_2$ under the experimental resolution, indicating that the position of the maxima is not affected by the length of the fluorinated chain.

The complete reaction mechanism according to the products observed is shown in Scheme 1. The photooxidation of

Scheme 1. Mechanism of Photooxidation of C$_6$F$_{13}$CH$_2$C(O)H

Figure 1. Infrared spectra obtained in the photooxidation of C$_6$F$_{13}$CH$_2$C(O)H in the presence of NO$_2$. From top to bottom: before photolysis; after 30 min irradiation; products; C$_6$F$_{13}$CH$_2$C(O)-OONO$_2$; and C$_6$F$_{13}$CH$_2$ONO$_2$. The last two traces correspond to reference spectra.

$C_6F_{13}CH_2C(O)H$ is initiated by the attack of chlorine atoms to the hydrogen atom of the aldehyde group to form $C_6F_{13}CH_2CO^\bullet$ radicals (reaction 1)[4]

$$C_6F_{13}CH_2C(O)H + Cl^\bullet \rightarrow C_6F_{13}CH_2CO^\bullet + HCl \quad (1)$$
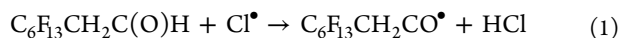
which follows a series of typical reactions occurring when O_2 and NO_2 are present, leading mainly to peroxynitrate and nitrate. The formation of the peroxynitrate is consistent with the relatively high concentration of NO_2, which reacts with the $C_6F_{13}CH_2C(O)OO^\bullet$ radical.

The formation of $C_6F_{13}CH_2ONO_2$ needs some explanation, however. $C_6F_{13}CH_2O^\bullet$ radicals could either react with either NO_2 or O_2 or decompose (reactions 2−4):

$$C_6F_{13}CH_2O^\bullet + O_2 \rightarrow C_6F_{13}C(O)H + HO_2^\bullet \quad (2)$$

$$C_6F_{13}CH_2O^\bullet + NO_2 \rightarrow C_6F_{13}CH_2ONO_2 \quad (3)$$

$$C_6F_{13}CH_2O^\bullet \rightarrow C_6F_{13}^\bullet + CH_2O \quad (4)$$
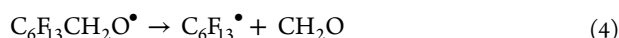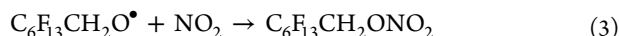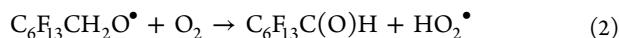
but given the scarcity of direct measurements for rate constants of long chain alkoxy radicals (>C4), those for reactions 2 and 3 have been assigned the values of 1×10^{-14} and 3×10^{-11} cm^3 molec^{-1} s^{-1}, respectively employing for the radical $C_6F_{13}CH_2O^\bullet$ a similar strategy as that used by Sulbaek Andersen et al.[16] for the $C_4F_9CH_2O$ radical using the database of Orlando et al.[21] Within this assumption, reaction 3 is favored under our experimental conditions. Furthermore, the formation of nitrate is observed in the infrared spectrum of the products shown in Figure 1, while the peak at 1777 cm^{-1} (corresponding to $C_6F_{13}C(O)H$)[4] is absent.

The unimolecular decomposition of the alkoxy radical does not compete effectively with reaction 2 at oxygen pressures higher than 7 mbar,[22,23] suggesting that formaldehyde will not be formed. This agrees with the nonobservation of their characteristic and intense infrared signals, which for our experimental conditions would impose a detection limit of 5.3×10^{-4} mbar.

Thermal Decomposition of $C_6F_{13}CH_2C(O)OONO_2$. The rate constant of the thermal decomposition of $C_6F_{13}CH_2C(O)OONO_2$ was experimentally measured at 9.0 mbar and 295 K. The peroxynitrate was introduced into the long path infrared gas cell, NO was added, and total pressure was obtained by the addition of N_2. The thermal decomposition of $C_6F_{13}CH_2C(O)OONO_2$ leads to the formation of peroxy radicals and NO_2 (reaction 5)

$$C_6F_{13}CH_2C(O)OONO_2 \rightarrow C_6F_{13}CH_2C(O)OO^\bullet + NO_2 \quad (5)$$
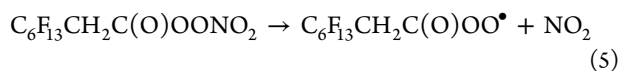
which could recombine through reaction -5

$$C_6F_{13}CH_2C(O)OO^\bullet + NO_2 \rightarrow C_6F_{13}CH_2C(O)OONO_2 \quad (-5)$$
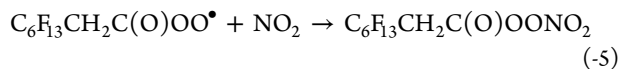
whose occurrence is prevented by the addition of NO, which effectively traps the peroxy radicals formed via reaction 6

$$C_6F_{13}CH_2C(O)OO^\bullet + NO \rightarrow C_6F_{13}CH_2C(O)O^\bullet + NO_2 \quad (6)$$
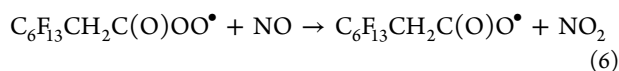
However, reaction 6 increases the concentration of NO_2 in the system, and reaction -5 begins to take significance as time elapses. Therefore, the measured effective first-order rate constant of decomposition (k_{obs}) is lower than the genuine unimolecular decomposition rate constant, k_5, so that eq 7 is required to obtain the genuine k.

$$k_5 = k_{obs}\left(1 + \frac{k_{-5}[NO_2]}{k_6[NO]}\right) \quad (7)$$

The ratio k_{-5}/k_6 was taken from that determined by Zabel et al. (1994),[24] who obtained a value of 0.64 for the $CF_3C(O)OO^\bullet$ radical. They also gave limiting values (0.4 and 0.8) accounting for the nature of the radical. The differences for the corrected rate constants using as ratio 0.64 and the limiting values is less than 4%, thus leaving the value chosen as a good approximation.

The value obtained for $k_5 = 1.2 \times 10^{-4}$ s^{-1} compares very well with those of other peroxynitrates having a methylene adjacent to the carbonyl group, that is, 1.5×10^{-4} s^{-1} for $CH_3CH_2C(O)OONO_2$[25] and our value of 1.6×10^{-4} s^{-1} for $CF_3CH_2C(O)OONO_2$ (see below). The characteristic peak at 1750 cm^{-1} was used to monitor peroxynitrate concentration and therefore determine k_{obs}.

Thermal Decomposition of $CF_3CH_2C(O)OONO_2$. The temperature dependence of the first-order rate constant was measured at two different pressures (9.0 and 1000 mbar) and temperatures ranging from 288 to 307 K. The decomposition

$$CF_3CH_2C(O)OONO_2 \rightarrow CF_3CH_2C(O)OO^\bullet + NO_2 \quad (8)$$

was carried out adding an excess of NO in the system sufficient to titrate the peroxy radicals formed

$$CF_3CH_2C(O)OO^\bullet + NO \rightarrow CF_3CH_2C(O)O^\bullet + NO_2 \quad (9)$$
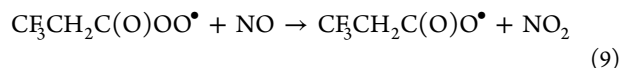
The experimental values obtained are plotted in Figure 2 and fitted with a linear regression to obtain the Arrhenius

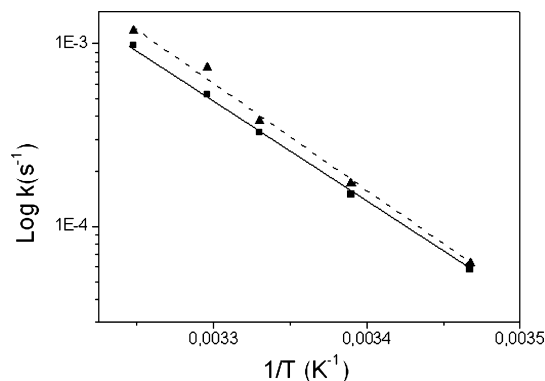**Figure 2.** Arrhenius plot for thermal decomposition of $CF_3CH_2C(O)OONO_2$. ■, 9.0 mbar; ▲, 1000 mbar.

parameters. Additional measurements of k_8 at 307 K show that the rate constant is dependent on the total pressure (Figure 3), and even at 1000 mbar the behavior is similar to the one shown for $CF_3C(O)OONO_2$ at 315 K.[24]

The Arrhenius parameters are presented in Table 2 and compared with those of similar fluorinated and hydrogenated peroxynitrates.

As it can be observed, the activation energy for $CF_3CH_2C(O)OONO_2$ decreases with total pressure (114 and 108 kJ/mol at 1000 and 9.0 mbar, respectively). It can also be seen that when an acyl-peroxynitrate is completely fluorinated (cf. rows 2 and 4) the activation energy increases beyond experimental uncertainty. Nevertheless, if the CF_3 group has a methylene bridging the carbonyl moiety, the former conclusion is not so
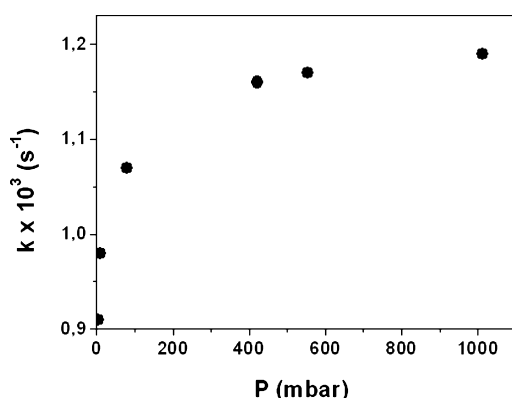
Figure 3. Pressure dependence of the rate constant for the thermal decomposition of $CF_3CH_2C(O)OONO_2$ (3.3 to 1000 mbar) at constant temperature (307 K).

Table 2. Kinetic Parameters for Selected Peroxynitrates at Different Pressures

total pressure = 1000 mbar			
peroxynitrate	E_a (kj/mol)	A (s^{-1})	ref.
$CF_3CH_2C(O)OONO_2$	114 ± 2	2.4 × 10^{16}	this work
$CH_3C(O)OONO_2$	113 ± 2	2.5 × 10^{16}	15
$CH_3CH_2C(O)OONO_2$	116 ± 2^a	7.2 × 10^{16}	25
$CF_3C(O)OONO_2$	119 ± 5	6.0 × 10^{16}	24
total pressure = 9.0 mbar			
peroxynitrate	E_a (kj/mol)	A (s^{-1})	ref.
$CF_3CH_2C(O)OONO_2$	108 ± 2^a	1.5 × 10^{15}	this work
$CH_3C(O)OONO_2$	106		15
$CH_3CH_2C(O)OONO_2$	107 ± 3	1.5 × 10^{15}	25^b

^{a}Uncertainty for the activation energy of $CF_3CH_2C(O)OONO_2$ was calculated from the fitting of the experimental data points of the rate constants used in the Arrhenius plot. ^{b}Measured at 11.5 mbar

clear because the difference in activation energies becomes on the order of the experimental uncertainty (cf. rows 1 and 3).

CONCLUSIONS

The results obtained have significant implications for understanding of the atmospheric oxidation mechanism of $C_6F_{13}CH_2C(O)H$, in the presence of O_2 and NO_2. The
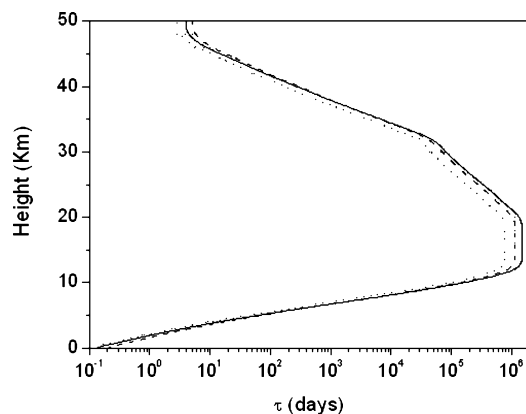
Figure 4. Atmospheric thermal lifetimes for $CH_3C(O)OONO_2$ (dotted line),[15] $CH_3CH_2C(O)OONO_2$ (dashed line),[25] and $CF_3CH_2C(O)OONO_2$ (solid line).

atmospheric fate of $C_6F_{13}CH_2C(O)H$ is reaction with OH radicals, leading to the formation of $C_6F_{13}CH_2C(O)OO^•$, which in an environment with high NO_2 concentrations could give $C_6F_{13}CH_2C(O)OONO_2$. The high stabilities of $C_xF_{2x+1}CH_2C(O)OONO_2$ (x = 1,6) that are similar to the stability of the most abundant peroxynitrates in the atmosphere (PAN, PPN), as Figure 4 shows, point out that the peroxynitrates formed from telomeric aldehydes can act as reservoir species for NO_2 and peroxy radicals in the atmosphere.

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Notes

The authors declare no competing financial interest.

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