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Henry's Law and Hydrolysis-Rate Constants for Peroxyacyl Nitrates (PANs) Using a Homogeneous Gas-Phase Source

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Abstract. The solubilities and hydrolysis rates of PAN (peroxyacetyl nitrate) and its homologues PPN (peroxypropionyl nitrate), PnBN (peroxy-*n*-butyl nitrate), PiBN (peroxy-isobutyl nitrate) and MPAN (peroxymethacryloyl nitrate) in liquid water have been studied at 20 °C. Temperature dependencies were measured for PAN and PPN. The solubilities of peroxyacyl nitrates decrease smoothly with increasing carbon-chain length from H (293 K) = 4.1 M atm^{-1} (PAN) to H (293 K) = 1.0 M atm^{-1} (PiBN). Hydrolysis-rate constants, which cover the range from k_h (293 K) = (2.4–7.4) × 10^{-4} s^{-1}, do not show a systematic chain-length dependency. Solubilities of PAN and PPN in solutions which mimic the composition and ionic strength of sea water are 15% and 20% lower than in pure water. The hydrolysis rate constants are not affected.

Key words: PAN, PPN, peroxyacyl nitrates, solubility, hydrolysis, salinity.

1. Introduction

The atmospheric photooxidation of hydrocarbons in the presence of NO_x leads, in addition to the net production of ozone and HNO_3, to the formation of organic nitrates and peroxy nitrates, which serve as temporary reservoirs for NO_2. Although a large variety of organic NO_y compounds are expected to be present in ambient air (Roberts, 1990), the peroxyacyl nitrates (PANs, $RC(O)OONO_2$) constitute the largest fraction of these species in the troposphere. The strong positive temperature dependence of the equilibrium $RC(O)OONO_2 \rightleftarrows RC(O)OO + NO_2$ (e.g. Bridier *et al.*, 1991; Roberts and Bertman, 1992) favours their long-range transport in cold air masses, particularly in the higher troposphere, and the release of NO_2 in warmer regions (Singh, 1987; Singh *et al.*, 1992). The formation pathways are well understood: the reaction of aldehydes with OH and the photolysis of ketones yields acyl radicals (RCO) which add O_2 and NO_2 to form PANs. Hydrocarbon emission inventories and oxidation schemes imply that peroxyacetyl nitrate (PAN, $R = CH_3$) is the most abundant peroxyacyl compound in the atmosphere, in good agreement with numerous field measurements (Roberts, 1990). The mixing ratios of peroxypropionyl nitrate (PPN, $R = C_2H_5$) were found to be 8–20% of PAN (Singh *et al.*, 1989; Grosjean *et al.*, 1993a). Recently peroxy-*n*-butyryl nitrate

(PnBN, R = C_3H_6) and peroxymethacryloyl nitrate (MPAN, R = $CH_2C(CH_3)$) have been identified and quantified in ambient air (Grosjean *et al.*, 1993a, b), the latter being attributed to the photooxidation of biogenic isoprene (Grosjean *et al.*, 1993c). Following the considerations of Grosjean *et al.* (1994c), butyl-substituted peroxyacyl nitrates in ambient air should amount to about 20% of the PAN mixing ratio. It is likely that other PANs like peroxy-isobutyryl nitrate (PiBN, R = $(CH_3)_2CH$), known to be a photooxidation product of gasoline vapour (Roumelis and Glavas, 1992), will also be detected in the environment.

This paper reports on aqueous solubilities (Henry's law constants) and hydrolysis-rate consltants of peroxyacyl nitrates at low concentrations. Such data are needed to quantify their interactions with cloud, fog, and seaspray droplets, and to assess the risk of loosing certain PANs on the wet surfaces of sampling devices.

2. Experimental

The peroxyacyl nitrates studied in this work were produced continuously in the gas phase using a photochemical reactor. The method is based on the preparation of peroxyacetyl nitrate (PAN) by the photolysis of acetone/NO_2/air mixtures at $\lambda = 254$ nm, as recently described in detail by Warneck and Zerbach (1992). A small flux of ketone vapour in N_2 was added to ~ 3.8 ppm NO_2 in air (from a permeation source), to achieve ketone mixing ratios of typically 3000 ppmv. Constant ketone mixing ratios were maintained by bubbling nitrogen through the liquid compounds at room temperature, and then passing the saturated carrier gas through a separator maintained at 20 °C. The ketone/NO_2/air mixture was fed to a 1-l Pyrex bulb, where it was irradiated by a low pressure mercury lamp (ozone-free type), as shown in Figure 1. Ketone photolysis is expected to yield acyl radicals (RCO), which add O_2 and NO_2 to form the respective peroxyacyl nitrate:

$$\mathrm{RCOR'} + h\nu \rightarrow \mathrm{RCO} + \mathrm{R'} \qquad (1)$$

$$\mathrm{RCO} + \mathrm{O_2} + \mathrm{M} \rightarrow \mathrm{RC(O)O_2} + \mathrm{M} \qquad (2)$$

$$\mathrm{RC(O)O_2} + \mathrm{NO_2} + \mathrm{M} \rightleftharpoons \mathrm{RC(O)OONO_2} + \mathrm{M}. \qquad (3)$$

We found, however, that under the experimental conditions employed in this work only acetone (R = R$'$ = CH_3) and 3-pentanone (R = R$'$ = C_2H_5) were efficient precursors of the expected photoproducts, peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN). Note that rather high mixing ratios of the ketones were necessry to yield sufficient amounts of acyl radicals during exposure times of only about 1.5 min. Therefore, only compounds with a high vapour pressure at room temperature could be used. Unsymmetrically substituted dialkyl ketones $R < R'$ (or ketones with another function X affixed to R$'$, like X = OH in hydroxyacetone) yielded only the shorter-chain (unsubstituted) peroxyacyl nitrates, RC(O)–ONO_2.

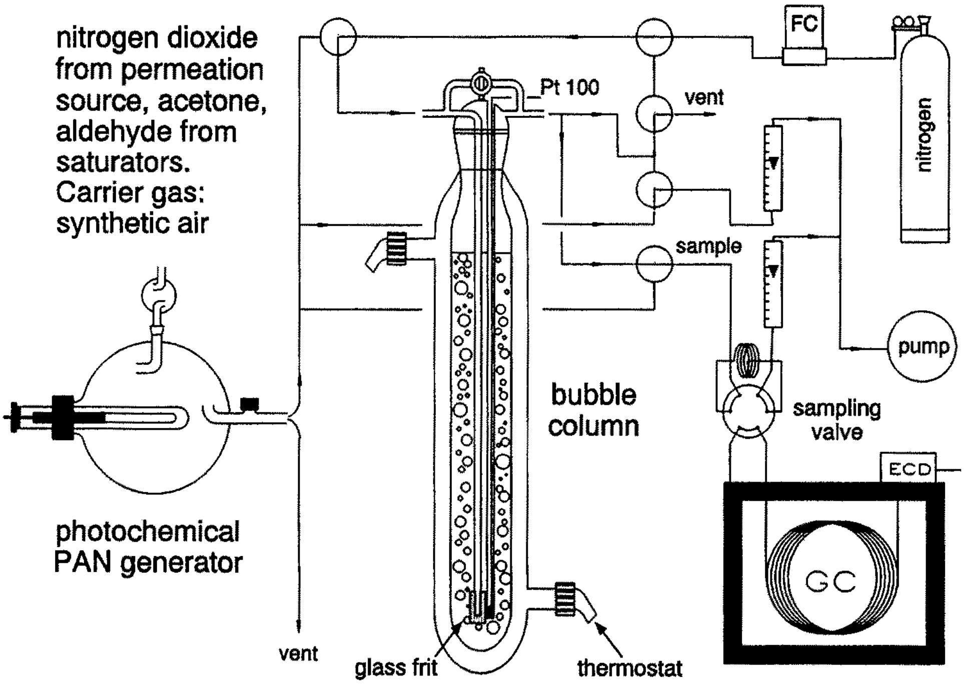

Fig. 1. Bubble-column apparatus, with photochemical PAN-generator after Warneck and Zerbach (1992).

Other peroxyacyl nitrates were synthesized by adding the vapour of a suitable parent aldehyde to the acetone/NO_2/air mixture. Peroxyacetyl radicals from the photolysis of acetone can either add NO_2, or abstract hydrogen from the aldehyde.

$$CH_3C(O)OO + RCHO \rightarrow CH_3C(O)OOH + RCO, \tag{4}$$

followed by reactions (2) and (3) of the RCO radical. This method yielded binary mixtures of PAN and $RC(O)OONO_2$.

PAN and PPN from the photolysis of NO_2/acetone/propanal in air were separated by gas chromatography on a 5-m HP-1 column, 530 μm i.d., and identified by comparing their retention times with those of the pure compounds, which were prepared by the nitration of peroxyacetic acid and peroxypropionic acid (Nielsen *et al.*, 1982). The identities of other PANs, which were analysed with NO_y-specific GC detectors (ECD, or a NO/O_3 chemiluminescence detector preceded by a $NO_y \rightarrow NO$ converter (Kames, 1992)), were checked by plotting $\log t_n$ (t_n = net retention time) versus alkyl-chain length, which yielded a straight line. Net retention times and capacity factors of the compounds studied in this work are listed in Table I for two column temperatures. Previous workers report that wide-bore columns are particularly suited for peroxyacyl nitrates analysis (Roberts *et al.*, 1989; Roumelis and Glavas, 1989). These columns combine good peak resolution

TABLE I. Net retention times $t_n = t_r - t_0$ and capacity factors $k' = t_n/t_0$ of 6 peroxyacyl nitrates at two column temperatures. 5-m HP-1 widebore column, 530 μm i.d., 2.65 μm film thickness, N_2 carrier gas, flow rate 8 ml min^{-1}. Peaks were detected with a dedicated NO/O_3 chemiluminescence analyser preceded by a CO/Au converter, void time 0.2 min

Compound	Column temperature (°C)	Net retention time t_n (min)	Capacity factor k' $k' = t_n/t_0$
PAN	30	1.0	5.0
(peroxyacetyl nitrate)	40	0.67	3.36
PPN	30	2.35	11.8
(peroxypropionyl nitrate)	40	1.52	7.6
PiBN	30	3.75	18.8
(peroxyisobutyryl nitrate)	40	2.37	11.9
MPAN	30	4.56	22.8
(peroxymethacryloyl nitrate)	40	2.86	14.3
PnBN	30	5.5	27.5
(peroxy-*n*-butyryl nitrate)	40	3.39	17.0
PVaN	40	8.2	41
(peroxyvaleryl nitrate)	45	6.4	32

capabilities with short retention times and low on-column losses of the thermally unstable PANs, due to the chemical inertness of the cross-linked polysiloxan phase. Another advantage of this type of column is their ability to resolve PAN from PiBN. These compounds are not separated on packed GC columns, which were traditionally used to measure PAN in ambient air (Grosjean *et al.*, 1994).

For the solubility and hydrolysis studies described below only the binary PAN-and-$RC(O)OONO_2$ mixtures were used, which were generated by the continuous photolysis of acetone/aldehyde/NO_2 mixtures. Good analytical results were obtained with peroxyacyl nitrate mixing ratios in the ppmv range, which required mixing ratios of typically 2500–5300 ppmv acetone and 1900–3500 ppmv aldehyde in the photochemical reactor. Since NO_y-specific GC-detectors were used, the large excess of unreacted acetone and aldehyde did not give rise to analytical problems. We also made sure that the accumulation of unreacted carbonyl compounds in the aqueous phase (typically much less than 0.1 M) did not affect the solubilities and hydrolysis rates of peroxyacyl nitrates within the range of our experimental conditions.

Due to the hydrolysis of peroxyacyl nitrates in aqueous solution (Lee, 1984; Holdren *et al.*, 1984; Kames *et al.*, 1991), Henry's law constants cannot be measured under static conditions, and a dynamic method must be chosen. Figure 1 shows the experimental setup with a bubble column which served as a gas–liquid reactor. The column consisted of a thermostatted silanized Pyrex tube of 2.8 cm i.d., height 30 cm, which was about 2/3 filled with water. The column temperature was measured

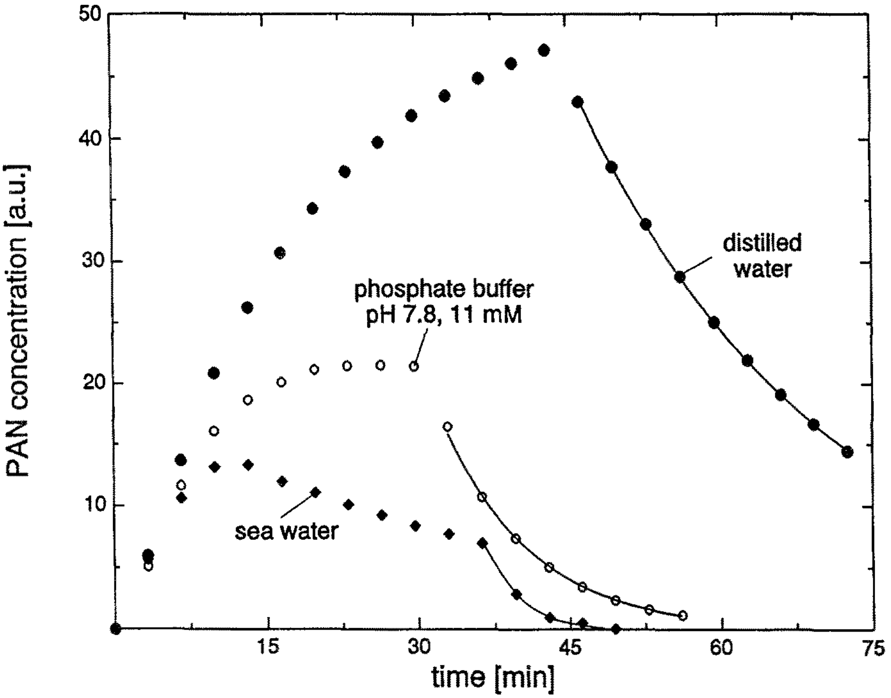

Fig. 2. PAN concentrations downstream of bubble-column during saturation and purge phases, $T = 293$ K, $V = 140$ ml, flow rates $\phi_{\mathrm{sat}} = 420$ ml min^{-1}, $\phi_{\mathrm{purge}} = 309$ ml min^{-1}; ●, distilled water; ○, phosphate-buffer solution; ♦, filtered North Sea water. Solid lines are first-order fits.

with an encapsuled Pt 100 resistor. Most experiments were carried out at a constant temperature of 293.2 ± 0.05 K. Temperature dependencies were studied in the range 273–298 K.

At the beginning of each experiment, the gas/liquid reactor was partially saturated with PAN and with the peroxyacyl nitrate under study. To this end, a constant fraction, typically 430 ml min^{-1}, of the photochemically generated gas mixture was sucked through a glass frit at the bottom of the bubble-column, as shown in Figure 1. Approach to saturation was monitored automatically by measuring the gas-phase concentrations of both peroxyacyl nitrates downstream of the bubble column at regular intervals, as shown in Figure 2, with a HP 5890 II gas chromatograph preceded by a timer-actuated six-port sampling valve. The compounds were separated on a 10-m HP-1 column, 530 μm i.d., and detected by an ECD.

When a suitable degree of saturation had been reached, the bubble column was switched from sample gas to pure humidified nitrogen. Purge gas-flow rates between 100 and 930 ml min^{-1} could be selected with a mass flow controller. The exponential decay of peroxyacyl nitrate concentrations in the bubble column due to the combined effect of purging and hydrolysis (cf. Fig. 2), was determined by measuring gas-phase concentrations downstream of the heterogeneous reactor, as previously described. Typical mixing ratios in the gas phase ranged from 400 ppbv to about 30 ppbv.

3. Results and Discussion

By varying the amount of water in the bubble column as well as the gas flow rate it was shown that equilibrium between PANs in solution and in the gas bubbles was always established under our experimental conditions. The first-order decay of PAN concentration c in the liquid phase due to purging and hydrolysis can thus be written as a simple function of the purge gas flow rate ϕ, the aqueous phase volume V, and the hydrolysis rate constant k_h:

$$-\frac{dc}{dt} = c\frac{\phi}{HV} + ck_h$$

$$\ln\frac{c_0}{c_t} = \left(\frac{\phi}{HV} + k_h\right)t = \ln\frac{c_{0,\ \mathrm{gas}}}{c_{t,\ \mathrm{gas}}}\,. \tag{5}$$

$$c = \text{aqueous phase concentration} = H\ \ c_{\mathrm{gas}}\,.$$

Figure 3 shows that semilog plots of $\ln(c_0/c_t)$ vs. time were indeed linear. By varying flow-to-volume ratios ϕ/V systematically and plotting the slopes of the pertaining semilog plots as functions of ϕ/V, Figure 4, Henry's law constants H and hydrolysis rate constants k_h of the PANs could be deduced from the slopes and intercepts of the resulting straight lines.

3.1. HENRY'S LAW AND HYDROLYSIS RATE CONSTANTS OF PANS IN PURE WATER

The results of our experiments in pure water at 293.2 K are summarized in Figure 4 and Table II. The most extensive data set was accumulated for peroxyacetyl nitrate (PAN), since it was always present in the photochemically generated binary mixtures of PANs.

Analogous to previously measured Henry's law constants of alkyl nitrates and bifunctional nitrates (Kames *et al.*, 1992), the solubilities of the peroxyacyl nitrates in water decrease systematically with increasing n-alkyl chain length. Note that the solubilities of PAN, PPN and PnBN differ by only a factor of two from the solubilities of the corresponding ethyl, n-propyl, and n-butyl acetates. This indicates that the solubilities of both classes of compounds are essentially due to solvation of the carboxylic function, while the attachment of the hydrophobic alkyl group (either at the carbonyl-carbon, or at the ester-oxygen) is unimportant. The chain-length dependence of the hydrolysis rate constants k_h is less obvious, and structural effects seem to be more important. The solubility of PAN determined in this work agrees well with previously published data (Lee, 1984; Kames *et al.*, 1991).

The temperature dependencies of H and k_h for the compounds PAN and PPN were measured in the range 1.5–24.5 °C. T-dependent raw data for PPN are

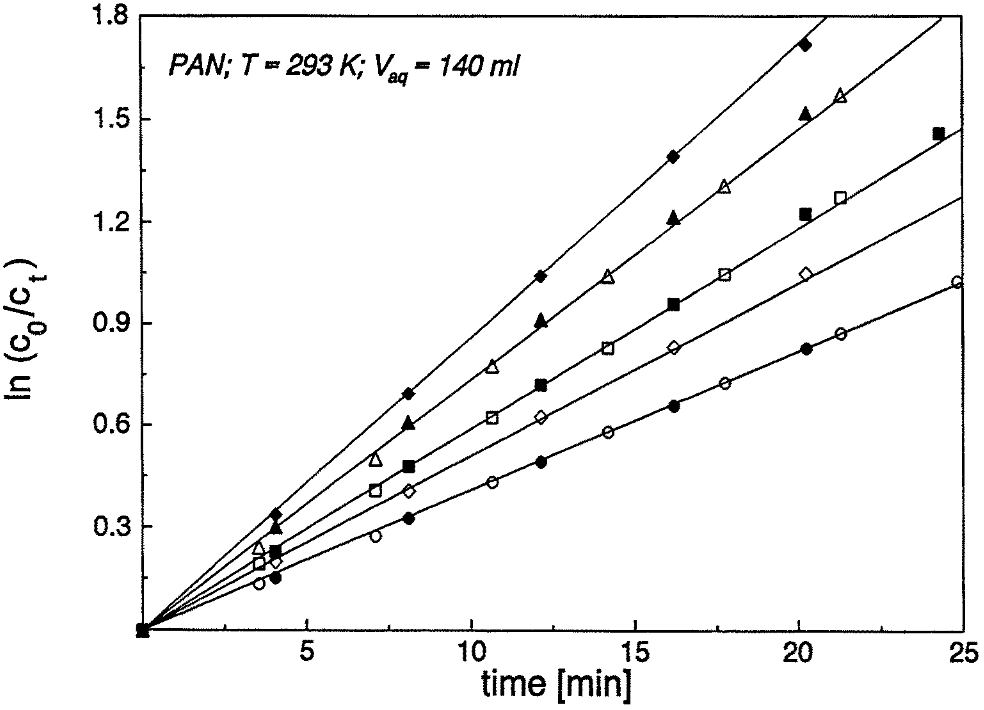

Fig. 3. Semilog plots for first-order loss of PAN from 140 ml distilled water, $\phi_{\text{purge}} = 276$, 435, 545, 756 and 916 ml min^{-1}.

displayed in Figure 5, which was constructed analogous to Figure 4. The corresponding semilog plots of ln H versus $1/T$ for PAN and PPN are shown in Figures 6 and 7, which include some literature data for comparison. Solvation enthalpies ΔH^0_{solv}, entropies ΔS^0_{solv}, activation energies E_a, and frequency factors A of H and k_h, respectively, were deduced from the plots by linear least-squares fitting. The obtained parameters, which are listed in Table III, may be used to estimate solubilities and hydrolysis rates outside the studied temperature range. The solvation enthalpies as well as the activation energies for the hydrolysis of PAN and PPN are the same within their error limits.

Figure 7 shows that the hydrolysis rate constants for PAN determined in this study, while being in reasonable agreement with results of other investigators (Lee, 1984; Holdren *et al.*, 1984), are systematically lower by about a factor of 1.6 at all temperatures than rate data previously reported by this laboratory (Kames *et al.*, 1991). The reason for the discrepancy is not clear. However, in view of the much better reproducibility of our present results, the lower hydrolysis-rate constants are considered more reliable.

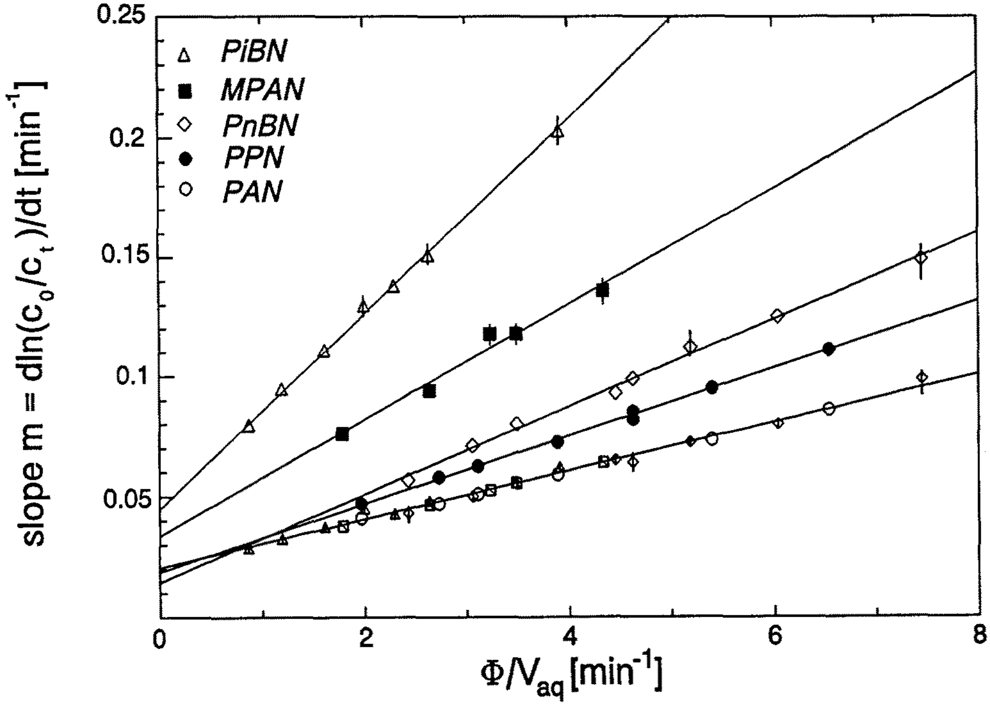

Fig. 4. First-order loss constants for PAN's in distilled water (T = 293 K, from semilog plots like shown in Fig. 3), plotted as function of ϕ/V.

3.2. SOLUBILITIES AND HYDROLYSIS-RATE CONSTANTS OF PAN AND PPN IN ELECTROLYTE SOLUTIONS

In order to assess the behaviour of PANs in the marine environment, we have attempted to measure the solubility of peroxyacetyl nitrate in authentic samples of filtered North Sea water, pH 7.8, ionic strength $I = \frac{1}{2}\Sigma z_i^2 c_i \approx 0.7$ M. However, instead of approaching saturation asymptotically, as was always the case in distilled water, the PAN concentration in the gas phase downstream of the bubble column passed through a low maximum after 12 min, whereafter it started to decrease, indicating a self-accelerating chemical loss process in North Sea water. The first order loss of PAN from the purged solution was also much faster than expected. In Figure 2, a North Sea water experiment (diamonds) is compared with a distilled water experiment (filled circles), and with an experiment in phosphate-buffer solution (open circles) which was carried out under identical experimental conditions as the sea water experiment (800 ppbv PAN in 420 ml min^{-1} feed gas, purge gas flow-to-volume ratio $\phi/V = 2.2$ min^{-1}, $T = 293$ K, pH 7.8), except for the lower ionic strength of the buffer solution.

The effect of salinity on the solubilities and hydrolysis rates of PAN and PPN was studied in a separate set of experiments with 'synthetic sea water' (solution of

TABLE II. Henry's law constants H (dimensionless), $\mathbf{H}$ [M atm^{-1}] and hydrolysis-rate constants k_h for PANs in distilled water ($\pm 1\sigma$ standard deviations). Data from this work, unless otherwise noted. Henry's law constants of acetic acid esters ($T = 295$ K) are included for comparison

Compound	H (293.2 K)	$\mathbf{H}$ (293.2 K) (M atm^{-1})	k_h (293.2 K) (10^{-4} s^{-1})
Peroxyacyl nitrates			
peroxyacetyl nitrate (PAN)	97.9 ± 2.0	4.1 ± 0.08	3.4 ± 0.14
	98.3 ± 4.8	4.1 ± 0.2	4.0 ± 1.2[a]
	97.4 ± 3.6	4.1 ± 0.15	6.4 ± 1.9[b]
	–	–	3.9 ± 0.9[c]
peroxypropionyl nitrate (PPN)	70.8 ± 1.5	2.9 ± 0.06	3.1 ± 0.22
peroxy-n-butyryl nitrate (PnBN)	54.8 ± 1.5	2.3 ± 0.06	2.4 ± 0.4
peroxymethacryloyl nitrate (MPAN)	41 ± 3.8	1.7 ± 0.16	5.6 ± 1.2
peroxy-isobutyryl nitrate (PiBN)	24 ± 0.7	1.0 ± 0.03	7.4 ± 0.5
Acetic acid esters			
ethyl acetate	187.7	7.8[d]	
n-propyl acetate	146.8	6.1[d]	
n-butyl acetate	117.9	4.9[d]	

[a] Lee, 1984, measurement at $T = 295$ K.
[b] Kames *et al.*, 1991.
[c] Holdren *et al.*, 1984.
[d] Kieckbusch and King, 1979.

TABLE III. Solvation enthalpies $\Delta H^0_{\mathrm{solv}}$, solvation entropies $\Delta S^0_{\mathrm{solv}}$, activation energies E_a, and preexponential factors A, fitting the observed temperature dependencies of H and k_h of PAN and PPN. Results from this work ($\pm 1\sigma$ standard deviations), unless otherwise noted

Compound	$\Delta H^0_{\mathrm{solv.}}$ (kJ mol^{-1})	$\Delta S^0_{\mathrm{solv.}}$ (J K^{-1} mol^{-1})	E_a (kJ mol^{-1})	A (s^{-1})
PAN	-47.4 ± 0.8	-150 ± 2.5	54.5 ± 0.5	$10^{(6.2 \pm 0.1)}$
	-49.2 ± 4.7	-157 ± 16	60.7 ± 11.7	$10^{(7.4 \pm 2.2)}$ [a, b]
	-54.2 ± 1.0	-173.1 ± 4	55.5 ± 5.5	$10^{(6.6 \pm 1)}$ [c]
PPN	-49.4 ± 0.9	-160 ± 3	54.4 ± 3.1	$10^{(6.2 \pm 0.6)}$

[a] $\Delta H^0_{\mathrm{solv.}}$ and $\Delta S^0_{\mathrm{solv.}}$ from Lee (1984).
[b] E_a and A from Holdren *et al.* (1984).
[c] Kames *et al.* (1991).

0.48 M NaCl, 0.03 M $CaCl_2$, and 0.03 M $MgSO_4$ in deionized water, simulating the composition and ionic strength $I = 0.69$ M of sea water; Schriever and Schuh, 1980). As shown in Table IV, the solubilities of both compounds were reduced by 15–20%. Similar salt effects, which have been explained e.g. by Masterton (1975)

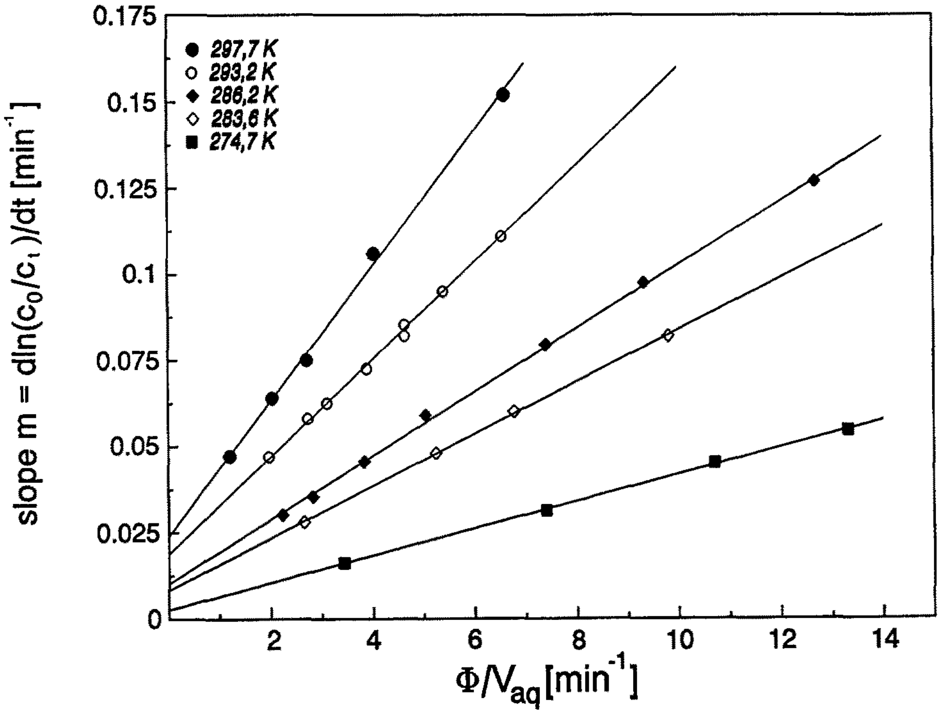

Fig. 5. First-order loss constants for PPN in distilled water (T = 297.7 K, 293.2 K, 286.2 K and 274.7 K, from semilog plots like shown in Fig. 3), plotted as function of ϕ/V.

on the basis of the *scaled particle theory*, have been reported for the solubilities of alkyl nitrates (Kames *et al.*, 1992). The hydrolysis-rate constants k_h of PAN and PPN were only insignificantly enhanced in 'synthetic sea water'.

According to these tests, the observed loss rate of PAN in North Sea water (Table IV), can not be accounted for by the salinity of the sample. Catalysis of PAN hydrolysis by OH^-, which was reported by Lee (1984), yields $k_{\mathrm{eff}} = k_h + k_{\mathrm{OH}} \times [\mathrm{OH}] \approx 4.4 \times 10^{-4}\ \mathrm{s}^{-1}$ at pH 7.8. This cannot explain the observed enhancement either. However, enhanced rates were observed both in this work (Fig. 2), and by Mudd (1966), for PAN hydrolysis in phosphate-buffer solutions (Table IV). It has in fact been proposed that the hydrolysis of certain *reactive esters* can be catalysed by nucleophilic anions (Kirby, 1972). While it was not possible to identify the species which are responsible for the fast decay of PAN in North Sea water, it is intereting to note that ozone deposition velocities on sea water have recently been reported to increase during periods of enhanced biological activity (McKay *et al.*, 1992). Whether both phenomena are related remains to be investigated.

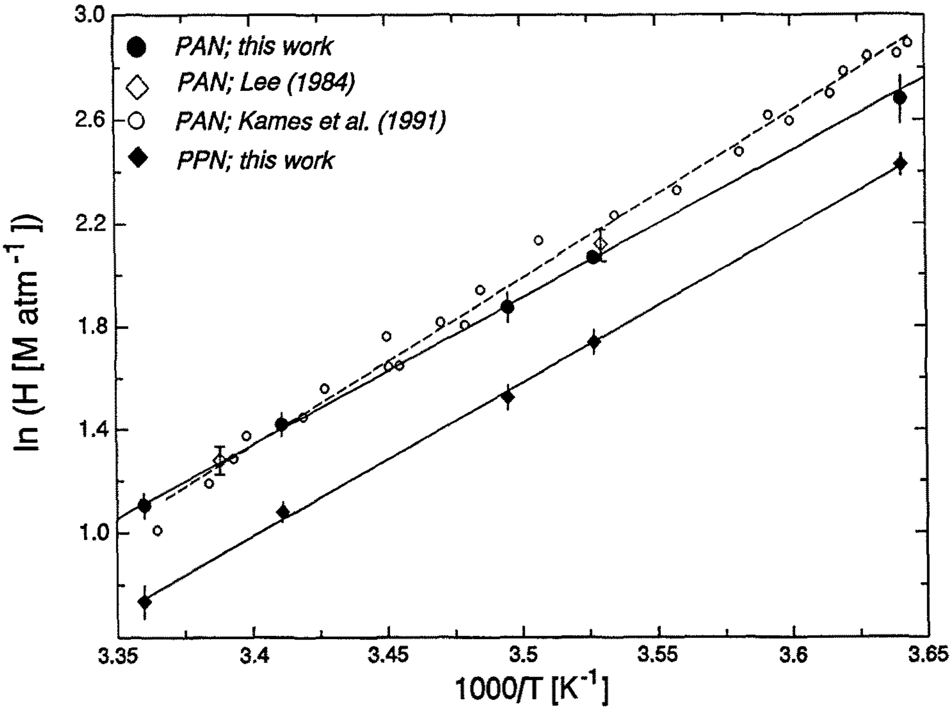

Fig. 6. Plot of $\ln H$ vs. $1000/T$ for ● PAN and ♦ PPN; error bars indicate total estimated error; comparison with literature data.

TABLE IV. Henry's law constants H (dimensionless), $\mathbf{H}$ [M atm^{-1}] and hydrolysis-rate constants k_h for PAN and PPN at 293 K in distilled water and in electrolyte solutions ($\pm 1\sigma$ standard deviations)

Compound	H (293.2 K)	$\mathbf{H}$ (293.2 K) (M atm^{-1})	k_h (293.2 K) (10^{-4} s^{-1})	Liquid-phase composition
Peroxyacetyl nitrate	97.9 ± 2.0	4.1 ± 0.08	3.4 ± 0.14	[a]
(PAN)	85.3 ± 3.7	3.6 ± 0.2	3.7 ± 0.4	[b]
	–	–	15.0	[c]
	–	–	33.0	[d]
	–	–	≈ 44 ± 7	[e]
Peroxypropionyl nitrate	70.8 ± 1.5	2.9 ± 0.06	3.1 ± 0.22	[a]
(PPN)	59 ± 9	2.5 ± 0.5	3.9 ± 0.2	[b]

[a] Distilled water, pH 6.8, this work.

[b] Synthetic sea water, ionic strength $I = 0.69$ M, this work.

[c] 11 mM phosphate-buffer solution, pH 7.8, this work.

[d] 33 mM phosphate-buffer solution, pH 7.2, from Mudd (1966).

[e] Filtered North Sea water, pH 7.8, this work, from Fig. 4.

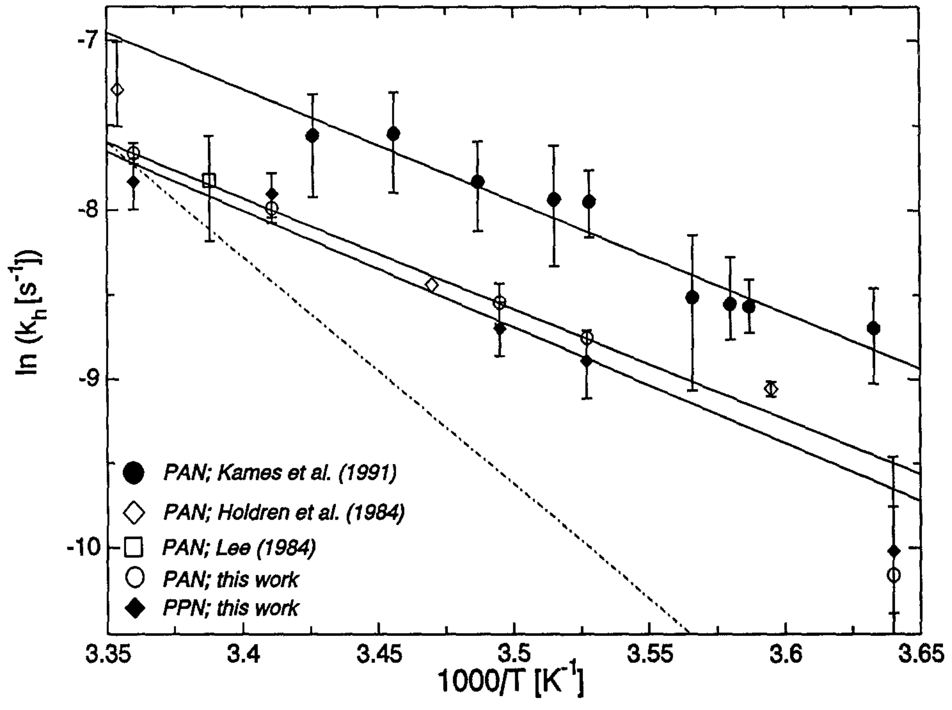

Fig. 7. Arrhenius plots of k_h for PAN and PPN in distilled water, comparison with literature data. Dashed line: temperature dependence of unimolecular PAN decay in the gas phase (Bridier *et al.*, 1991).

4. Conclusions

The 254-nm photolysis of acetone/NO_2 mixtures in air, which was introduced by Warneck and Zerbach (1992) as a clean source of PAN, can be transformed into a flexible *binary* source of PAN and other peroxyacyl nitrates, by simply adding suitable precursor aldehydes to the acetone/NO_2 mixture. PANs which are difficult to prepare by other methods, can thus be synthesized under field conditions, e.g. for species identification in ambient air samples by comparison of GC retention times.

The continuous photochemical source of peroxyacyl nitrates has been utilized to determine Henry's law constants and hydrolysis-rate constants of five PANs in deionized water. Previous results for PAN were confirmed. The data can be used to assess the fate of PANs in contact with cloud and fog droplets. Mass-transport considerations (Schwartz, 1986) imply that the gas/liquid phase equilibrium between cloud droplets and interstitial air will be rapidly established in the atmosphere. In the *phase-mixed limit*, which applies to trace gases with low solubilities and slow hydrolysis rates like the PANs studied in this work, the removal rate in cloud droplets becomes a simple function of the liquid water content of the cloud, $L = V_{\mathrm{aq}}/V_{\mathrm{air}}$:

$$\mathit{First\text{-}order\ removal\ rate} = k_h H L. \qquad (6)$$

For typical clouds, $L \approx 5 \times 10^{-7}$. The life-times of PANs with respect to this loss mechanism would thus amount to 2–5 years, showing that this loss process is entirely negligible. This is in accordance with observations of Cox and Penkett (1982), who found that PAN mixing ratios in the atmosphere were unaffected by rainfall (work cited by Høv, 1984).

Very small deposition velocities of PAN, $v_{\mathrm{D}} \approx 0.005$ cm s^{-1}, have previously been measured on a stagnant water surface (Schurath *et al.*, 1984). More recently, v_{D} of PAN on a flat water surface was shown to be hydrolysis-rate controlled, being proportional to $\sqrt{k_h}$ (Kames *et al.*, 1991). Therefore, a tenfold enhancement of the hydrolysis rate in sea water, Table IV, will not give rise to a very significant lifetime reduction of PANs in the marine environment. The life-time of PANs is controlled by the fast reaction between NO and RC(O)OO, which exists in a strongly temperature-dependent equilibrium with NO_2 and $RC(O)OONO_2$.

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