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Synthesis of Peroxyacetyl and Peroxyaroyl Nitrates. Complexation of Perqxyacetyl Nitrate with Benzene

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Table II. Comparison of Quantum Yield Factors Using Initial Conditions of Zafonte et al. (*3*) and Reaction Scheme from Table I

initial NO_2, ppm	initial NO, ppm	Δt, s	ϕ (this work)	ϕ (ref 3)	difference, %
		Research-Grade Nitrogen, 0.5 ppm of O_2			
4.0	<0.01	1	1.81	1.68	7.7
4.0	<0.01	5	1.78	1.68	6.0
4.0	<0.01	10	1.74	1.68	3.6
2.5	0.15	1	1.74	1.61	8.1
2.5	0.15	5	1.71	1.61	6.2
2.5	0.15	10	1.68	1.61	4.3
1.0	0.30	1	1.57	1.54	1.9
1.0	0.30	5	1.56	1.54	1.3
1.0	0.30	10	1.54	1.54	0.0
		Extra-Dry Nitrogen, 300 ppm of O_2			
4.0	<0.01	1	1.74	1.68	3.6
4.0	<0.01	5	1.70	1.68	1.2
4.0	<0.01	10	1.64	1.68	−2.4
2.5	0.15	1	1.63	1.61	1.2
2.5	0.15	5	1.59	1.61	−1.2
2.5	0.15	10	1.53	1.61	−5.0
1.0	0.30	1	1.40	1.54	−9.1
1.0	0.30	5	1.34	1.54	−13.0
1.0	0.30	10	1.27	1.54	−17.5

$j(NO_2)$ measurements (5%), the effect of the initial tube must be less than 1.7%, as predicted by Zafonte et al. (*3*).

Discussion

One of the most important results of these new calculations is the dependence of the quantum yields on exposure time, as shown on Table II. Commercial NO_x detectors often have a time lag due to the volume of the plumbing between sample inlet and reaction chamber. This time lag can be as long as 30 s, and during this time the composition of the sampled gas can change. For example, if $j(NO_2)$ is measured in "extra-dry" N_2 by using the mean initial conditions described previously, a 30-s delay will reduce the apparent $j(NO_2)$ by ~5%. Thus measurements of $j(NO_2)$ in N_2 should include careful consideration of trace O_2 content, N_2O_5 chemistry, and exposure time effects on quantum yield. The new quantum yield, 1.69 ± 0.08, is accurate to at least 5% for O_2 contents from 0 to 50 ppm. Alternatively, measurements should be made in air or O_2 with a NO_x detector modified to give appropriately fast response (*2*).

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Synthesis of Peroxyacetyl and Peroxyaroyl Nitrates. Complexation of Peroxyacetyl Nitrate with Benzene

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■ Convenient procedures are given for the condensed-phase synthesis of peroxyacetyl nitrate (PAN), peroxybenzoyl nitrate, and *m*-chloroperoxybenzoyl nitrate from the corresponding peracids, sulfuric acid, and sodium nitrate. The position of the ^1H NMR signal from peroxyacetyl nitrate in CCl_4–benzene mixtures depended on the solvent composition in a way consistent with complex formation between PAN and benzene, with K_{eq} = 0.095 at 27 °C.

Peroxyacyl and peroxyaroyl nitrates are highly reactive compounds of considerable interest because of their physiological and chemical action in polluted atmospheres (*1–4*). Samples of such compounds are routinely needed for calibration of analytical instruments for their detection, and several syntheses have been published (*1, 5–8*). The procedure of Louw et al. (*5*) is particularly convenient because the reaction is carried out in the condensed phase, although rather corrosive reagents are required.

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Stephens (*1*) reported that mixtures of nitric and sulfuric acids gave only traces of peroxyacetyl nitrate (PAN) from peracetic acid. We find, however, that yields of PAN comparable to those from other procedures in the condensed phase (*5*) can be obtained from peracetic acid with sulfuric acid when the nitric acid is produced in situ by addition of sodium nitrate or (in initial experiments) anhydrous calcium nitrate (Table I). The method works equally well for the conversion of two peroxybenzoic acids to the corresponding peroxybenzoyl nitrates.

Experimental Section

A typical procedure was as follows. A 50-mL 3-necked flask equipped with an inlet for nitrogen, a thermometer, and a magnetic stirring bar was flushed with N_2 and charged with 30 mL of nitrogen-flushed pentane (Burdick and Jackson). The flushing of the flask with nitrogen could be omitted if the room air was relatively dry. The flask was placed in an acetone bath, and its contents were stirred under nitrogen while sufficient dry ice was added to the bath to cool the pentane to 0 °C. Peracetic acid (40% in acetic acid, FMC Corp., 4.0 mmol) was added with stirring at this temperature, followed by concentrated sulfuric acid (3.6 g, 2.0 mL) and then finely powdered sodium nitrate (0.85 g, 10 mmol, Baker) at a rate such that the temperature remained <5 °C (**Caution! Exotherm!**). After stirring at 0 °C for 30 min, the mixture was poured onto ~30 g of ice in a separatory funnel and shaken until the ice had melted. The lower layer was separated, and the organic layer was washed three times with 30 mL of ice water and dried over anhydrous $MgSO_4$. The IR spectrum of the solution displayed strong bands (*1*) from PAN at 1830 and 1725 cm^{-1} and no absorptions in the OH stretching region or from other carbonyl species.

Solutions of PAN in pentane or hexane, prepared in this manner, have been stored over $MgSO_4$ at −18 °C for several months without evidence of significant decomposition (IR). A new peak in the gas chromatogram of a pentane solution did appear on standing under these conditions, and the intensity of this peak grew with time. Its retention time was nearly coincident with that of PAN under our column conditions, and the retention time was identical with that of a synthetic sample of 2-pentyl nitrate (*9*). Solutions in carbon tetrachloride, on the other hand, were qualitatively observed to be much less stable under the same storage conditions, although the reasons for this difference are not known.

Table I. Conditions for Synthesis of PANs

precursor,[a] g	solvent, mL	H_2SO_4, mL	$NaNO_3$, g	temp	time	yield, %
40% CH_3CO_3H in CH_3COOH						
0.76	*n*-pentane, 30	2.0	0.85	0	30 min	35–40
1.54	CCl_4, 60	4.3	1.71	−5	30 min	35
0.60	chlorobenzene, 30	3.9	1.7	−5	30 min	0
80% *m*-chloroperbenzoic acid[b]						
1.58	*n*-pentane, 30	5.6	2.31	−10	3 h	33
1.15	CCl_4, 50	1.03	0.408	−10	3 h	30
perbenzoic acid[c]						
0.096	*n*-pentane, 20	0.31	0.39	−20	3 h	45

[a] Weights are given for the amount of pure peracid present. [b] Aldrich. The remaining 20% of the material is largely *m*-chlorobenzoic acid. [c] From benzoyl chloride and H_2O_2 (*16*). The aqueous peracid product was extracted into pentane.

For calibration purposes, PAN was transferred from the pentane by bubbling dry N_2 through the solution into a Teflon bag. The concentration in the bag was determined by Fourier transform infrared analysis (*10, 11*) (pentane spectrum substracted) with a 1.0-m cell. Simultaneously, samples of PAN were withdrawn from the bag with glass/Teflon gas-tight syringes and diluted with a known volume of clean air in a second, evacuated Teflon bag. Multiple dilutions were used to derive a calibration curve concentration vs. detector response in the gas chromatogram (*4*). Losses of PAN either in the original or in diluted bags were detectable over a few hours, although substantial losses have been observed over a weekend (cf. ref *10*). The pentane solution could also be injected directly onto the chromatographic column for analysis.

The concentration of PAN in solution was measured by addition of an aliquot of solution (30–60 μL) to excess 3 M KOH, followed by colorimetric (*11, 12*) analysis of the extract for nitrite ion. Analysis by iodometric methods gave values ca. 20% higher than with this method, but the results were not very reproducible. The concentration of PAN in carbon tetrachloride could also be determined conveniently by addition of a known amount of benzene to a weighed aliquot followed by comparison of the integrated peak heights of PAN and the standard by NMR. We have not attempted to isolate the PAN from solution (*1, 7*).

No PAN was formed by our procedure when chlorobenzene was the solvent, and perbenzoic acid itself did not yield any peroxybenzoyl nitrate under the conditions described above. We reasoned that both of these results were due to a competitive, oxidative attack on aromatic rings by the peracid moiety under strongly acid conditions. A reasonable yield of peroxybenzoyl nitrate was then subsequently obtained simply by changing the order of addition, so that the peracid was added to the other ingredients stirred at −20 °C. Under these conditions, the destructive side reactions are not competitive with the desired reaction (Table I).

The washed and dried ($MgSO_4$) organic solutions of the peroxyaroyl nitrates showed only infrared absorptions which could be ascribed to solvent and to the desired products. In particular, they were free from aromatic acid (ν_{CO} at ~1700 cm^{-1}) and anhydride (ν_{CO} ~1770 cm^{-1}). One preparation of peroxybenzoyl nitrate contained an impurity with ν = 1760 cm^{-1}, which was removed by concentrating the solution under reduced pressure and below 25 °C to an oil, and selectively extracting the desired product by stirring with *n*-pentane at −20 °C. The aromatic PANs do not appear to be prone to sudden decomposition, although they were never stored in the pure state, and handled with suitable care in amounts less than 200 mg.

The yields of peroxyaroyl nitrates were determined by evaporating the solvent from an aliquot at aspirator pressure and weighing the residue. The absence of decomposition during this procedure was established by dissolution of the residue in the original volume of solvent and by comparison of the IR spectra (*5*) of the original and reconstitued solutions.

NMR spectra were recorded at ambient temperature with a Varian EMI-360. Chemical shifts were measured downfield from internal tetramethylsilane.

Discussion

Nicksic et al. (*13*) reported values of 78 and 137.5 cps, respectively, for the H NMR chemical shifts of PAN in benzene and carbon tetrachloride. The magnitude of this difference surprised us and suggested that the signal in one case may have been due to a decomposition product. Nicksic's assignments are correct, however. We found that the chemical shift of the methyl group decreased regularly when a solution 0.045 M in CCl_4 was diluted progressively with benzene (Figure 1).

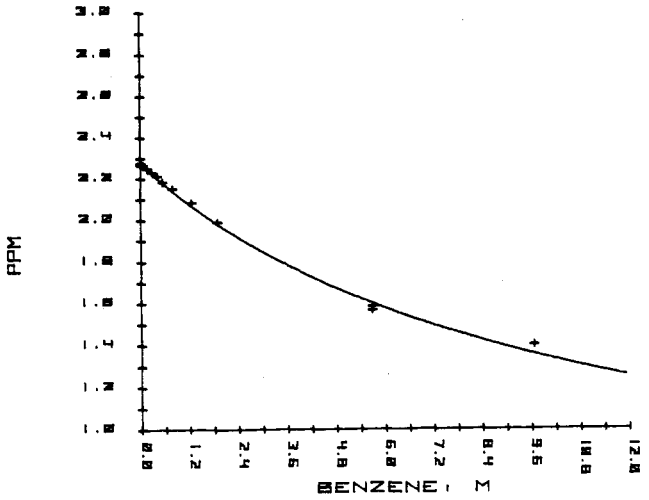

Figure 1. Proton chemical shift of peroxyacetyl nitrate (initially 0.045 M in carbon tetrachloride) as a function of added benzene at 27 °C.

The data were analyzed by standard methods (*14, 15*)

$$C_6H_6 + CH_3COO\text{-}ONO_2 \rightleftarrows \text{complex}$$
$$2.28 \text{ ppm} \qquad \lambda \text{ ppm}$$

with the assumption that the observed signal position represented an average of free and complexed PAN. The curve through the points in Figure 1 corresponds to the least-squares fit of the data to the equation $(\delta_{obsd} - \delta_{CCl_4})/(\text{benzene}) = K_{eq}\lambda - K_{eq}\delta_{obsd}$, which gave $K_{eq} = 0.095\ M^{-1}$ and $\lambda = 0.356$ ppm. The observed value of the methyl resonance in pure carbon tetrachloride ($\delta_{CCl_4} = 228$ ppm) and the calculated value in pure benzene at 11.2 M (1.288 ppm) correspond to shifts of 136.8 and 77.3 cps, respectively, for a 60-MHz instrument. These values are in good agreement with the reported ones (*13*). The upfield shift of the methyl resonance is presumably due to deshielding of the methyl protons in a face-centered complex by the π-orbitals of the benzene molecule. Similar phenomena have been observed from the H NMR spectra of benzene–acetonitrile mixtures (*17*). The resonances of PAN were very sharp at all concentrations of benzene, implying a complex with $t \lesssim 10^{-7}$ s, which is consistent with the small value of K_{eq}. Upfield shifts of the methyl resonance were also obtained with benzene-d_6 in place of benzene.

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