aldehyde (106 mg, 1.00 mmol), 1% cross-linked phosphine polymer 1 (400 mg, 1.00 mmol), and CCl_4 (5 mL) were stirred under reflux under nitrogen for 4 h. The polymer was filtered off and washed in the usual way. GLC analysis of the products (with an SE-30 stationary phase at 180 °C) indicated the presence of benzal chloride (50 mg, 62% of the theoretical maximum), β,β-dichlorostyrene (52 mg, 60% of the theoretical maximum), and benzaldehyde (11 mg, 10% recovered).

Reactions Summarized in Table VI and Figures 1 and 2. A mixture of the substrate (1.00 mmol) and phosphine (2.00 mmol) in CCl_4 (10 or 30 mL as indicated in the table) was vigorously stirred in a stoppered reaction tube (1 in. wide × 4 in. deep) immersed above the level of the solvent in a thermostated (±0.5 °C) oil bath. For reactions monitored by GLC the 1% cross-linked polymer used contained 2.50 mmol of phosphine/g, and the linear polymer used contained 2.42 mmol of phosphine/g. For reactions monitored by HPLC the 1% cross-linked polymer used contained 2.42 mmol of phosphine/g, and the linear polymer used contained 2.69 mmol of phosphine/g. For reactions monitored by IR spectroscopy the 1% cross-linked polymer contained 2.50 mmol of phosphine/g. Periodically (see Figures 1 and 2 as examples) small samples (<0.05 mL) were removed from the reaction mixtures and analyzed by GLC, HPLC, or IR spectroscopy as indicated in Table VI. When reactions were monitored by GLC, a small known amount of β-methylnaphthalene was added to the reaction mixture to serve as an internal standard. IR analyses were carried out by comparing the areas of the carbonyl peaks in the 1650–1900-cm^{-1} region due to carboxylic acid and acyl chloride. Each reaction was carried out at least twice. The yields of alkyl chloride from a given reaction were found to be reproducible to ±5% of the values given. The yields of acyl chloride from a given reaction were reproducible to ±20% of the values given.

Acknowledgment. We thank the SERC for financial support.

Registry No. Octan-1-ol, 111-87-5; hexadecan-1-ol, 36653-82-4; octadecan-1-ol, 112-92-5; 3-phenylpropan-1-ol, 122-97-4; 4,4,4-triphenylbutan-1-ol, 16778-07-7; 5β-cholan-24-ol, 3110-99-4; 2-*n*-butoxyethanol, 111-76-2; 4-(hydroxymethyl)-2,2-dimethyldioxolane, 100-79-8; cinnamyl alcohol, 104-54-1; benzyl alcohol, 100-51-6; *p*-chlorobenzyl alcohol, 873-76-7; octan-2-ol, 123-96-6; cyclohexanol, 108-93-0; octadecanethiol, 2885-00-9; 3-phenylpropanethiol, 24734-68-7; phenylmethanethiol, 100-53-8; *n*-octanoic acid, 124-07-2; phenylacetic acid, 103-82-2; stearic acid, 57-11-4; phenoxyacetic acid, 122-59-8; 3-*O*-acetyllithocholic acid, 4057-84-5; cinnamic acid, 621-82-9; benzoic acid, 65-85-0; β-naphthoic acid, 93-09-4; α-furoic acid, 88-14-2; aniline, 62-53-3; *p*-toluidine, 106-49-0.

Decomposition Rates, Synthesis, and Spectral Properties of a Series of Alkyl Hyponitrites

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A number of *trans*-alkyl hyponitrites (RON=NOR) were synthesized and characterized. At 66.1 ± 0.1 °C in isooctane and with millimolar to micromolar concentrations first-order kinetics were observed with half-lives (min) of 12.8 ± 0.2 (CH_3), 32.3 ± 1.1 (2-C_3H_7), 15.0 ± 0.3 (cyclohexyl), 25.2 ± 1.2 (*tert*-butyl), 18.3 ± 0.3 (*tert*-pentyl), 3.0 ± 0.1 (benzyl), 11.2 ± 0.5 (2-phenylethyl), and 5.5 ± 0.3 (1-phenylethyl). The rate constants were concentration independent and showed little change with changes in solvent polarity or viscosity. Ultraviolet, magnetic resonance, infrared, and mass spectra for the new hyponitrites are reported. Most of the hyponitrites were highly crystalline solids that could be stored for long periods without change below 0 °C.

Introduction

Organic hyponitrites are convenient, low-temperature thermal and photochemical sources of alkoxyl radicals.[1] With the exception of benzyl hyponitrite,[3] there are virtually no quantitative studies of the rates of decomposition of the nontertiary alkyl esters in the literature,[4] and only sporadic information concerning their spectral properties. Recently an X-ray structure determination and an analysis of the vibrational spectra of *tert*-butyl hyponitrite were reported.[2b] In the present work we present the synthesis, decomposition rates and products, and additional spectral data on the lower alkyl hyponitrites.

Experimental Section

For chemiluminescence studies, water from a constant-temperature bath (Poly Temp Model 80) circulated through the jacket of a Pyrex cell containing the sample in 4–6 mL of solvent. The reaction cell contained a cap provided with inlet and exit tubes to permit flushing the sample with nitrogen and with a well extending to the bottom of the cell for a thermocouple wire. The cell was contained in a blackened box 6 in. on a side. One side of the box had an opening through which light was detected with a Hamamatsu Model R562 PMT, operated at 950 V in a PRF Model TE104TSRF constant-temperature housing. The housing as purchased contained a built-in amplifier–dicriminator. Data were recorded at appropriate intervals (40–150 s) in the photon-counting mode with a HP5316A frequency counter and an Omega Model 410A digital thermometer, both of which were integrated with an Apple II computer for data storage in text files and subsequent analysis.

Kinetic studies by HPLC were carried out with solutions of hyponitrites in 10- or 25-mL volumetric flasks immersed in the constant temperature bath. Aliquots were periodically withdrawn

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(1) A number of references to the hyponitrite literature were given in two recent papers.[2] This paper was presented at the 186th ACS National Meeting, March 20–25, 1983.

(2) (a) Mendenhall, G. D.; Stewart, L. C.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5109–14. (b) Ogle, C. A.; VanderKooi, K. A.; Mendenhall, G. D.; Lorprayoon, V.; Cornilsen, B. C. *J. Am. Chem. Soc.* **1982**, *104*, 5114–9.

(3) (a) Ho, S. K.; de Sousa, J. B. *J. Chem. Soc.* **1961**, 1788–97. (b) De Sousa, J. B. *Nature (London)* **1963**, *199*, 64–5. (c) Ray, N. H. *J. Chem. Soc.* **1969**, 4023–8.

(4) Rate studies of cyclohexyl hyponitrite have been carried out by UV and chemiluminescence methods: Druliner, J. D.; Domaille, P. J.; Krusic, P. J.; Tolman, C. A.; Mendenhall, G. D. Presentation at the Industrial and Engineering division, ACS Annual Meeting, Washington, D.C., September, 1979.

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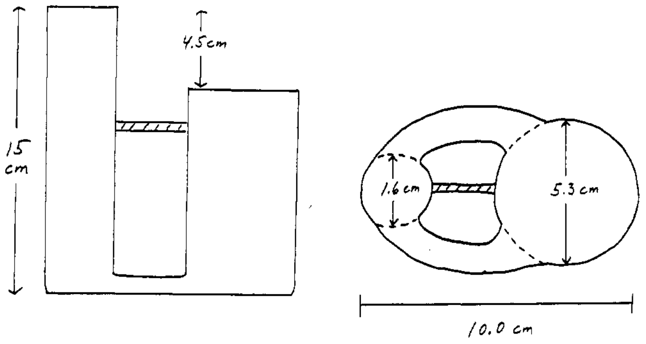

Figure 1. Apparatus drawing.

and placed in 1-mL vials that were crimp-sealed and stored in ice.

Liquid chromatography of the aliquots was performed with a Hewlett-Packard 1084B liquid chromatograph equipped with an HP79850B-LC terminal. Injection volumes of at least 10 μL were eluted through a RP-18, 10-μm column obtained from Hewlett-Packard with acetonitrile–water mixtures and detected at 240 or 255 nm.

Analysis of the chemiluminescence data was carried out with a modification of the program CURFIT.[5] Generally the fit to first-order kinetics was made over 4–12 half-lives by optimizing the F statistic by varying the background counting rate that was subtracted out of the data. The correlation coefficients of the semilogarithmic fits to the data obtained by both chemiluminescence and HPLC methods after reaching temperature equilibration were >0.98 in every case and usually >0.99.

Product studies were carried out in all but one case with 2–5-mL samples that were sealed in Pyrex tubes after degassing by freeze–thaw techniques. Most of the gas chromatographic analyses were carried out with a Perkin-Elmer Sigma 3 and a 6 ft × $^1/_4$ in. column packed with Carbowax 400 on 60/80 Chromasorb P. Magnetic resonance spectra were recorded with a Varian EMI360 or other commercial instruments. The UV spectra were recorded with samples in spectrograde solvents on a Perkin-Elmer Lamda-3. Most IR spectra were recorded with a Perkin-Elmer Model 283, and mass spectra with a Hewlett-Packard Model HP 5985 or equivalent spectrometer. The DSC measurement was carried out with a Du Pont Model 1090 instrument. Combustion analyses were performed by Mr. Frank Huber at Battelle Laboratories. Exact masses were determined at the Midwest Center for Mass Spectrometry, University of Nebraska.

Sodium hyponitrite was prepared from sodium and nitric oxide by a method described by one of us earlier or by an earlier modification with pyridine,[6] from sodium amalgam and sodium nitrite,[7] from alkyl nitrites and hydroxylamine,[8] or by electrolysis of sodium nitrite.[9] The last method, which avoids use of metallic sodium, was convenient to carry out for small quantities with the glass apparatus shown in Figure 1.

The aqueous solutions in the tubes were isolated by a pool of Hg that was stirred magnetically in the larger one. The anode was a spool of nickel wire (80 g, 0.025 in. diameter) which was suspended in concentrated aqueous NaOH in the larger tube. A nickel wire, immersed in the mercury cathode to complete the circuit, was insulated from the aqueous solution with a glass tube. The narrow compartment typically contained 5 g of $NaNO_2$ as a 33% solution and was reduced completely after several hours of operation (4 V, 2–4 A). To avoid decomposition of the hyponitrite, the entire apparatus was contained in an ice bath. The reduced solution was worked up by precipitating sodium hyponitrite (5–10% yield) with ethanol or silver hyponitrite with silver ion as described elsewhere.[6,7,9]

Silver hyponitrite was prepared as described previously[6] and stored below 0 °C in the dark. The compound was generally stable for months under these conditions, although the stability of individual preparations showed considerable variation. On two occasions we obtained material that was not sensitive to light. The reasons for this departure from usual experience were not obvious.

Methyl Hyponitrite. Silver hyponitrite (1.78 g, 6.45 mmol) was added in small portions at 25 °C to a stirred mixture of methyl iodide (0.80 mL, 12.9 mmol) and pentane (4 mL). After stirring 2.5 h, the solution was filtered and the solids were washed with a little pentane. The filtrate was washed successively with 95% hydrazine (2 mL) and water (3 × 5 mL) and dried (Na_2SO_4). The resulting solution (4.8 mL) showed a singlet at δ 3.9 (^1H NMR); integration with respect to an added sample of acetophenone indicated a concentration of 0.14 M (14%). A few drops of the solution were injected into an evacuated gas cell. An intense absorption appeared at 1070 cm^{-1} with a shoulder at 1075 cm^{-1}. The other bands in the spectrum were weak and could not be distinguished from solvent absorptions. Mass spectral data and an alternate synthesis are given elsewhere.[10]

2-Propyl Hyponitrite. Silver hyponitrite (2.9 g, 7.3 mmol) was added in portions to 2-propyl bromide (10 mL) stirred at 0 °C, and then allowed to stir overnight at 25 °C and filtered. The filtrate and washings were combined, and about a third of the volume was concentrated (0 °C, <20 torr) to a yellow oil that crystallized. Recrystallization could be accomplished from methanol at −78 °C. **Caution**: The neat hyponitrite detonated violently when struck. The compound melted around 0 °C to a fragrant liquid. The yield was about 80% (NMR method); mass spectrum (CH_4–NH_3), m/e (major) 164 ($M + NH_4^+$), 147 ($M + H^+$), 116, 101, 99, 88, 85, 75, 71; ^1H NMR (C_2Cl_4) δ 1.3 (d, 6 H J = 6 Hz), 4.52 (spt, 1 H, J = 6 Hz); IR (neat) 2970 s, 2920 m, 2870 m, 1450 w, 1464 m, 1380 s, 1340 m, 1150 s, 1120 s, 995 vs, 904 w, 820 m cm^{-1}.

***n*-Butyl Hyponitrite.** n-Butyl iodide (2.1 mmol, 0.38 g, $NaHSO_3$-washed and redistilled) was added to a slurry of silver hyponitrite (2.3 mmol, 0.63 g) in benzene (2 mL). The mixture was stirred in the dark at 25 °C for 5 h and allowed to stand 3 days at 8 °C. The yellow slurry was filtered and the yellow precipitate was washed with benzene. The colorless filtrate was washed with hydrazine (2 mL) and water (3 × 50 mL) and dried (Na_2SO_4). Concentration (<20 torr) gave a brown liquid which was eluted through a pad of silica gel with n-pentane. Removal of solvent <20 torr afforded a colorless liquid (0.05 g, 28%); ^1H NMR ($CDCl_3$) δ 4.25 (t, 1 H), 0.6–1.9 (m, 7 H); IR (neat) 2950 s, 2860 s, 1465 m, 1375 m, 1330 w, 1295 w, 1255 w, 1230 w, 1110 w, 1065 s, 1055 s, 1035 s, 1025 s, 1110 s, 990 m, 970 m, 925 m, 830 w, 730 w cm^{-1}; mass spectrum (EI), m/e (major) 175 ($M + H^+$), 119 (impurity?), 91, 88, 75, 71, 58, 57, 55, 43.

1-Phenylethyl hyponitrite was prepared from 1-phenylethyl bromide (1.36 g 7.35 mmol, Chemical Procurement Co.) in pentane (10 mL) by addition of silver hyponitrite (1.0 g) portionwise with stirring at 0 °C followed by stirring 1 h after removal of the cold bath. Filtration and cooling to −78 °C led to 0.21 g (22%) of colorless crystals, mp 72–73 °C dec (from methanol). Anal. Found: C, 71.0; H, 6.8; N, 10.7. ^1H NMR ($CDCl_3$) δ 1.58 (d, 6 H, 7 Hz), 5.40 (q, 1 H, 7 Hz), 7.32 (s, 5 H); mass spectrum (CH_4–NH_3), (major) m/e 288 ($M + NH_4^+$), 271 ($M + H^+$), 260, 140, 138, 122, 105, 88, 75; (EI) (major) m/e 122–120, 107–105, 91, 79–77, 63, 51, 43. IR (KBr) 3180 w, 3000 w, 2980 m, 2930 w, 1490 s, 1450 s, 1372 s, 1352 s, 1310 m, 1287 m, 1212 m, 1123 w, 1080 sh, 1071 s, 1031 m, 1008 s, 997 s, 982 s, 919 m, 870 m, 845 w, 759 s, 701 s, 629 s, 613 m, 595 s, 512 w cm^{-1}.

2-Phenylethyl iodide was prepared by stirring 2-phenylethyl bromide (150 g, Chemical Procurement Co.) overnight with sodium iodide (300 g) and acetone (500 mL). The organic liquid was washed with water, dried ($MgSO_4$), and passed through a column of alumina with pentane eluant. The organic solvents were removed <20 torr to give an oil (135 g) that was used without further purification.

2-Phenylethyl hyponitrite was prepared by adding dry silver hyponitrite (2.76 g) to the above iodide (4.6 g) in stirred ether

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[5] CURFIT appears in a disk that accompanies the text "Basic Microcomputer in Biology", by Spain, J. D.; Addison-Wesley Publishing Company, Advanced Book Division: Reading, MA, 1981.

[6] References and a cautionary note appear in 2a.

[7] Neumann, R. C., Jr. Bussey, R. J. *J. Am. Chem. Soc.* **1970**, *92*, 2440–5.

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[10] Mendenhall, G. D.; Cary, L. W. *J. Org. Chem.* **1975**, *40*, 1646–7.

Table I. Spectral Data for Alkyl Hyponitrites

alkyl group	λ_{max}, nm	ϵ_{max}	solvent	$\nu_{CO/NO}^{-1}$, cm^{-1}
methyl				1070 (gas)
isopropyl	224.2	7540	heptane	995 (neat)
n-butyl				1025 (neat)
cyclohexyl	226.0	7180	heptane	992, 1014 (KBr)
tert-butyl	224.6	7010	heptane	990[a] (KBr)
tert-butyl	226.6	6760	35% H_2O in CH_3CN	
tert-amyl	225.1	7000	isooctane	990 (neat)
2-phenylethyl				1030 (KBr)

[a] Reference 2b.

(5 mL) followed by 3.5 h at reflux. Filtration and cooling to −78 °C gave colorless crystals (0.25 g, 9%) that were filtered off and recrystallized from methanol, mp 55 °C dec. Anal. Calcd: C; 71.1, H, 6.7; N, 10.4. Found: C, 71.0; H, 6.8; N, 10.7. Mass spectrum (CH_4–NH_3), *m/e* 288 (P + 18), 260, 230, 200, 140, 122, 108; (EI), *m/e* 182, 179, 165, 122, 105, 104, 92, 91, 77, 65, 63, 51. A small parent ion appeared at *m/e* 270. ^1H NMR ($CDCl_3$) δ 3.01 (t, 2 H, *J* = 7 Hz), 4.43 (t, 2 H, *J* = 7 Hz), 7.28 (s, 5 H). IR (KBr) 2962 w, 2948 w, 2882 w, 1600 w, 1492 m, 1478 m, 1452 m, 1378 m, 1201 w, 1030 s, 940 s, 750 s, 698 s, 596 s, 579 m, 484 w cm^{-1}.

Cyclohexyl hyponitrite was prepared in a similar manner in 25% yield from cyclohexyl bromide and silver hyponitrite in hexanes. The product crystallized at −78 °C from the filtered reaction mixture, mp 79–80 °C dec (from methanol); IR (KBr) 2930 s, 2850 s, 1502 m, 1365 m, 1350 m, 1245 w, 1040 s, 1015 s, 992 s, 930 m, 920 m, 889 m, 797 w, 615 s, 518 m; ^1H NMR ($CDCl_3$) δ 1.0–2.3 (br s, 20 H), 4.3 (br s, 2 H); exact mass (M + H$^+$), 227.17475.

***tert*-Butyl** and ***tert*-pentyl hyponitrites** were prepared by methods described elsewhere.[11-13] The latter showed ^1H NMR ($CFCl_3$) δ 0.90 (3 H, distorted t), 1.30 (s, 6 H), 1.79 (distorted q, 2 H); IR (neat) 2960 s, 2930 m, 2870 w, 1430 m, 1382 m, 1370 m, 1300 w, 1250 m, 1205 m, 1179 m, 1158 m, 1068 w, 990 s, 860 w, 790 w, 750 w cm^{-1}; mass spectrum (EI), *m/e* 202 (small), 172, 103–101, 71 ($C_5H_{11}^+$), 59, 55, 53, 43, 41, 39; exact mass (M + H$^+$), 203.1786.

Results

Preparation and Properties. The alkyl hyponitrites could be prepared readily from silver hyponitrite and excess alkyl bromide or stoichiometric bromide or iodide in a volatile solvent, generally depending on whether the halide itself was volatile or not. The yields, which were not optimized, were low in some cases probably because of competing elimination reactions. Most hyponitrites were highly crystalline solids that were stable indefinitely below 0 °C. Methyl hyponitrite, which explodes spontaneously when purified,[10] was handled only in solution. Isopropyl hyponitrite exploded only when deliberately struck, although it is more stable kinetically than the widely used *tert*-butyl ester. The lower members volatilize readily and have very pleasant odors, but *tert*-pentyl hyponitrite could not be distilled by the bulb-to-bulb technique at 1 torr. The IR and UV spectra of hyponitrites were recorded, and spectral data for several of them appear in Table I.[14] All showed an intense, broad band near 1000 cm^{-1}, which has been assigned to the overlap of asymmetric C–O and N–O stretching modes.[2b] This characteristic band was observed to shift progressively from 990–995 cm^{-1} in tertiary hyponitrites to 995–1014 cm^{-1} in secondary hyponitrites, to 1020 cm^{-1} in primary hyponitrites, and to 1070 cm^{-1} in methyl hyponitrite. In other hyponitrites not included in Table I, a number of strong bands were also observed in the same spectral region, but we could not assign any one specifically to the hyponitrite group.

The UV spectra of saturated hyponitrites are quite insensitive to substituents and, for *tert*-butyl, to solvent polarity. The extinction coefficient of the *tert*-butyl ester in isooctane is close to a reported[15] value of 7130 ± 40 at 223.4 nm in pentane. The lack of solvent shift and the magnitude of the values of ϵ are consistent with an assignment of a π–π^* transition to the band.

Kinetic Studies. The rates of decomposition of the hyponitrites were measured by following the loss of starting material in aliquots by high-pressure liquid chromatography, and more conveniently by monitoring the chemiluminescence emission from the solutions in the presence of 9,10-dibromoanthracene (DBA).[16] The former method is more general, since solutions of tertiary hyponitrites or of 2-phenylethyl hyponitrite did not chemiluminescence. Since solvent-derived radicals in solutions of alkyl hyponitrites can react with oxygen to give peroxy radicals which also chemiluminesce upon termination,[17] the chemiluminescence was followed only in nitrogen-flushed solutions. Initial concentrations of hyponitrite were below 10^{-3} M in order to minimize induced decomposition from radicals or excited states. The results are summarized in Table II.

The kinetic runs analyzed by HPLC methods were carried out in air-saturated solutions. Most of the runs with non-tertiary hyponitrites were each repeated in the presence of the antioxidant octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate (Irganox 1076). None of the replicate experiments with and without antioxidant showed significant difference in rate constants. Methyl hyponitrite, which is quite volatile, was examined only by the chemiluminescence technique. The rate constants at 66.1 °C were averaged after correcting the ones obtained at temperatures ±0.1 °C from this value with the Arrhenius equation and an assumed activation energy of 28 kcal/mol. The averages were converted to the half-lives given in the abstract. The two rate constants for methyl hyponitrite obtained at the lowest concentration were not used in the calculation, because the values were obtained with very weakly chemiluminescing solutions.

Our rate constants generally agree well with reported ones from previous determinations of hyponitrite esters. From data given by Kiefer and Traylor for di-*tert*-butyl hyponitrite in isooctane,[11] we calculated log $k_d = 15.08 - (28600/\theta)$, which gives $k_d = 4.54 \times 10^{-4}$ s^{-1} at 66.1 °C, compared with our value of 4.57×10^{-4} s^{-1}. Cyclohexyl hyponitrite in cyclohexane at 66.1 °C has a rate constant for decomposition[19] of 8.3×10^{-4} s^{-1}, similar to our value of $(7.7 \pm 0.2) \times 10^{-4}$ s^{-1} in isooctane. From a rate constant

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[15] Kenley, R. A. Ph.D. Thesis, University of California, San Diego, 1973.

[16] This compound is widely used as a triplet acceptor.[17,18]

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[18] Wilson, T.; Golan, D. E.; Harris, M. S.; Baumstark, A. L. *J. Am. Chem. Soc.*, **1976**, *98*, 1086–91 and references therein.

[19] Interpolated from data of reference 4.

Table II. Rate Constants for Decomposition of Alkyl Hyponitrites

alkyl	$R_2O_2N_2$, 10^4 M (init.)[a]	T, °C (±0.1 °C)	$10^4 k$, sec^{-1}	method, solvent[d]
CH_3	1.38	66.0	7.8, 8.0	CL, isooctane
	4.06	66.1	8.9	same[b]
	12.1	66.1	9.1	same[b]
i-C_3H_7	10.0	66.1	3.4	HPLC, isooctane
	10.0	66.1	3.5	same, 14 mM inh
	0.096	66.1	3.7	CL, isooctane
	0.96	66.2	3.7	same
	0.96	66.1	3.7	same
	5.76	66.2	3.56	same
	3.8	66.1	3.4	CL, dimethylformamide
			3.6 ± 0.1	(avg)
n-C_4H_9	0.15	66.1	7.7	CL, isooctane
	0.15	66.2	8.1	same
	1.48	66.0	8.0, 7.8	same
	1.48	66.1	8.2	same
	9.15	66.1	8.3	HPLC, isooctane
	9.15	66.1	8.1	same, 10^{-2} M inh
			8.0 ± 0.2	(avg)
c-C_6H_{12}	0.92	66.1	7.5	CL, n-heptane
	0.906	66.1	7.6	CL, isooctane
	0.906	66.1	7.6	same
	10.8	65.5	6.9, 7.2	HPLC, isooctane
	10.8	66.1	7.7	same, 1.1 mM inh
	11.4	66.1	8.0	same, 2.85 mM inh
			7.7 ± 0.2	(avg)
t-C_4H_9	12.7	66.1	4.57	HPLC, isooctane, 2.55 mM inh
t-C_5H_{11}	18.7	66.1	6.3	HPLC, isooctane
$PhCH_2$	4.18	55.5	10.8	CL, benzene[c]
	0.43	55.5	11.0	same
	0.61	55.5	10.7	CL, isooctane
	0.61	55.5	10.3	CL, tetradecane
	0.61	55.5	11	CL, white oil
	1.6	66.1	39	CL, isooctane
	1.6	66.2	39	same
			39 ± 1	(avg)
$PhCH_2CH_2$	11.2	66.1	10.4	HPLC, isooctane
	10	66.1	9.6	same
	10	66.1	9.7	same, 10^{-4} M inh
	1	66.1	10.9	same, 10^{-5} M inh
	11	66.1	10.2	same, 10^{-2} M inh
	10.3	66.1	10.8	HPLC, 95% ethanol
			10.2 ± 0.5	(avg)
$PhCH(CH_3)$	11.7	66.1	20	HPLC, isooctane
	11.7	66.1	20	same, 10^{-2} M inh
	2.3	66.1	22	CL, isooctane
	0.22	66.1	21 ± 1	(avg)

[a] 0.0012 M DBA (added as 0.032 M stock solution in benzene) present in run by CL method unless otherwise noted. [b] DBA = 0.0018 M. [c] DBA = 0.032 M. [d] inh is Irganox 1076 (see text).

and an activation energy for benzyl hyponitrite decomposition in cyclohexane given by Ho and de Sousa,[3a] we calculate $\log k_d = 13.865 - (25330/\theta)$, which gives $k_d = 3.5 \times 10^{-3}$ s^{-1} at 66.1 °C, in satisfactory agreement with our determination of 3.9×10^{-3} s^{-1} in isooctane at this temperature. Neumann and Lind's data[20] for this compound in benzene at 30–50 °C lead to $\log k_d = 9.814 - (19400/\theta)$, which extrapolates to $k_d = 2.08 \times 10^{-3}$ s^{-1} at 66.1 °C. Ray[3c] also measured decomposition rates for this ester at 89–123 °C in liquid paraffin by a calorimetric method. His data lead to the expression $\log k_d = 8.068 - (15460/\theta)$ with $r = -0.998$. In spite of the linearity of this relationship, the values of activation energy and of log A are anomalously low. We predict from this expression $k_d = 1.29 \times 10^{-2}$ s^{-1} at 66.1 °C, which is over a factor of 3 higher than the rate constants in similar solvents described above.

Products of Decomposition. We analyzed decomposed solutions of some of the alkyl hyponitrites in alkanes for the expected alcohols and for some other products corresponding to recombination, dismutation, or β-scission of the alkoxy radicals. The results of these studies are given in Table III.

Table III. Decomposition Products from Alkyl Hyponitrites

hyponitrite	conditions	products, M
isopropyl	a	0.32 i-C_3H_7OH, 0.039 acetone
$tert$-butyl	b	0.16 t-C_4H_9OH, 0.013 $(t\text{-}C_4H_9)_2O_2$, 0.0018 acetone
n-butyl	b	0.051 n-C_4H_9OH, 0.006 n-butyraldehyde
cyclohexyl	b	0.10 cyclohexanol, 0.051 cyclohexanone
$tert$-pentyl	b	0.148 acetone, 0.022 $tert$-pentanol
1-phenylethyl	c	0.15 $PhCHOHCH_3$, 0.060 $PhCOCH_3$
2-phenylethyl	b	0.088 $PhCH_2CH_2OH$, 0.064 $PhCH_2CHO$, 0.016 toluene, 0.0041 $(PhCH_2)_2$

[a] 0.22 M in n-decane, injected into GC port at 200 °C. [b] 0.10 M isooctane 48 h at 45 °C. [c] 0.11 M in isooctane 20 h at 50 °C.

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Calorimetry. A DSC study of 2-phenylethyl hyponitrite was carried out with a 2.9-mg sample and a heating rate giving 10 °C/min. A melting endotherm with $\Delta H = -427$ cal/g appeared with a minimum at 54.4 °C followed by a broad decomposition exotherm with $\Delta H = 4807$ cal/g, which maximized at 89.4 °C and returned to the base line at 110 °C. The curve was not analyzed further because of the complicated nature of the product mixture.

Discussion

The most interesting result of the study was the absence of induced decomposition for dilute solutions of primary and secondary alkyl hyponitrites. In none of several solvents in Table II was there clear evidence of a rate acceleration at concentrations up to 10^{-3} M. The clean, first-order kinetics observed is actually expected upon estimation of the reactivity of the alkoxyl radicals produced from decomposition. As an example, consider the decomposition of isopropyl hyponitrite in neat (6.0 M) isooctane. From recent work[21] we calculate the rate of H abstraction by *tert*-butoxyl from cyclopentane as 8.4×10^5 M^{-1} s^{-1} at 25 °C. From this value we can calculate the rate constant toward our solvent isooctane by assuming a 1:10:44 reactivity ratio[22] of *tert*-butoxyl toward primary, secondary, and tertiary alkane hydrogens. This leads to a value of 4.0×10^6 M^{-1} s^{-1}. If the rate of attack on isooctane by 2-propoxyl is similar (it will probably be slightly faster[2a]) and if we similarly equate the abstraction of the methine hydrogen of 2-propanol by *tert*-butoxyl[23] (1.8×10^6 M^{-1} sec^{-1}) to the abstraction of the methine hydrogen of isopropyl hyponitrite by isopropoxyl, we can readily estimate that for 10^{-3} M hyponitrite the pseudo-first order rate constant for attack of 2-propoxyl on solvent will be about $6.0 \times 4 \times 10^6 = 2.4 \times 10^7$ s^{-1}, but for attack on 2-propyl hyponitrite only $10^{-3} \times 1.8 \times 10^6 \times 2$ H/mol $= 3.6 \times 10^3$ s^{-1}. The H abstraction from solvent will produce carbon-contered radicals and then (in air) peroxy radicals, but these are still less reactive than alkoxyls. There is conclusive evidence for induced attack on benzyl hyponitrite by trimethyltin radicals, however, although the site of attack is at the azo linkage rather than at a CH bond.[20]

The shock sensitivity of the hyponitrites decreases with increasing molecular weight, as expected, and we could not detonate esters with alkyl groups containing six or more carbon atoms. Simple dilution with solvent is sufficient to lessen the sensitivity of the lower members of the series. The aromatic hyponitrites were handled with no special precautions, even for the DSC experiment.

The decomposition rates of hyponitrite esters at constant temperature (Table II) increase generally with the inductive electron-withdrawing ability of the alkyl group. A plot of the rate constants for the aliphatic hyponitrites of this study against the polar substituent parameter[25] σ^*, which was derived from ionic reactions, illustrates this trend although the relationship is not very linear (Figure 2). This rather weak substituent effect was found in two series of aromatic hyponitrites as well.[3b,24]

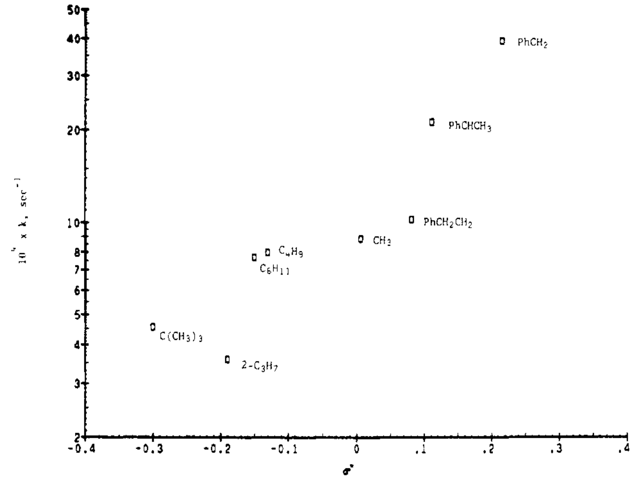

Figure 2. Logarithms of alkyl hyponitrite decomposition rate constants at 66.1 °C vs. σ^*.

The use of chemiluminescence emission for measurement of the decomposition rates of hyponitrites is extremely convenient and gives values that are satisfactorily close to those obtained by more laborious chromatographic methods. The rate constants for decomposition of cyclohexyl hyponitrite in cyclohexane also showed good agreement between UV and chemiluminescence methods.[4] In this context we would point out an early, qualitative gas-phase study of the chemiluminescence from ethyl hyponitrite–acetaldehyde mixtures, which was ascribed to excited biacetyl.[26] The nature and quantum yields of excited states formed in the condensed phase from hyponitrites are currently under investigation.[27] The mechanism for their production is through disproportion of geminate pairs of alkoxyl radicals:

$$R_2CHON{=}NOR' \rightarrow [R_2CHO\cdot + N_2 + \cdot OR']_{cage} \rightarrow R'OH + R_2CO\ (^0S, {}^1S, {}^3T)$$

Since experimental[7] evidence favors a concerted mechanism in the initial step, it is reasonable that the light emission following the relatively rapid production of excited states and energy transfer steps will then be proportional to the rate of hyponitrite decomposition. This should be true regardless of the complexity of the subsequent reactions, as long as they are all first order or pseudo first order, and the composition and optical properties of the medium do not change significantly.

The mass balance among the products (Table III) was not very satisfactory in several cases, presumably because of attack of cage-escaped alkoxyls or solvent-derived radicals with decomposition products or because of other reactions. These reactions would be more important than in the kinetic studies, which were carried out at lower concentrations. Similarly, Newmann and Lind found 48% benzyl alcohol, only 25% benzaldehyde, and 5% benzyl benzoate from 0.2 M benzyl hyponitrite in benzene,[20] whereas Partington and Shah isolated benzaldehyde phenylhydrazone in 78% yield from this hyponitrite by trapping the aldehyde product in situ with phenylhydrazine in ethanol.[28] The product distribution from *tert*-butyl hyponitrite agreed well with that found in earlier work.[11] On the other hand, Walling and McGuinness[12] decomposed *tert*-amyl hyponitrite in mixtures of toluene, chlorobenzene, and cyclohexane, and obtained *tert*-pentanol to acetone ratios of 2–5, over an order of magnitude higher than our ratio of 0.15. Perhaps the aromatic sol-

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vents retard the β-scission of this alkoxyl.

Finally, in the case of 2-phenylethyl hyponitrite, we may assume that the excess of alcohol over aldehyde (0.024 M) in the product mixture represents the amount of alkoxyls which abstracted a hydrogen atom from the medium rather than from another caged alkoxyl. The sum of β-scission products (toluene plus 2(bibenzyl)) is also 0.024 M and suggests that the rate constants for β-scission and H abstraction from solvent are comparable. A recent determination[2a] led to $k_{\text{scission}} = 3.7 \times 10^7\ \text{sec}^{-1}$ in benzene at 45 °C for this alkoxyl. We estimated the pseudo-first-order decay of *tert*-butoxyl in isooctane as $2.5 \times 10^7\ \text{s}^{-1}$ (vide infra). The 2-phenylethoxyl radical is about 3 times more reactive in H abstraction toward benzhydrol than *tert*-butoxyl,[2a] which brings the agreement between calculated rates for scission and abstraction to within a factor of 2 if the reactivities of the two alkoxyls toward isooctane are similarly related.

Conclusion

trans-Alkyl hyponitrites represent a well-behaved class of compounds whose decomposition rates are less subject to induced decomposition and solvent effects than some other sources of radicals. The shock sensitivity of the compounds disappears on dilution. The major sources of sample loss appear to be volatilization, which affects hyponitrites with alkyl groups as large as *tert*-butyl,[29,30] and adventitious photosensitized decomposition in aromatic solvents or of hyponitrites with aromatic rings.

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Registry No. Methyl hyponitrite, 86886-15-9; isopropyl hyponitrite, 86886-16-0; *n*-butyl hyponitrite, 86886-17-1; cyclohexyl hyponitrite, 86886-18-2; *tert*-butyl hyponitrite, 82554-97-0; *tert*-amyl hyponitrite, 85972-35-6; 2-phenylethyl hyponitrite, 86886-19-3; benzyl hyponitrite, 86886-20-6; 1-phenylethyl hyponitrite, 82522-46-1; silver hyponitrite, 7784-04-5; methyl iodide, 74-88-4; 2-propyl bromide, 75-26-3; *n*-butyl iodide, 542-69-8; 1-phenylethyl bromide, 585-71-7; 2-phenylethyl iodide, 17376-04-4; 2-phenylethyl bromide, 103-63-9; cyclohexyl bromide, 108-85-0.

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[30] Early workers were unable to distill the lower hyponitrites at reduced pressure, although this was presumably due to their thermal decomposition.[28]

Reactivity of Superoxide Ion with Ethyl Pyruvate, α-Diketones, and Benzil in Dimethylformamide

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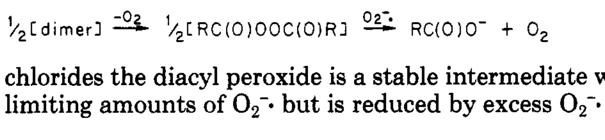
The dominant net reaction of $O_2^{-}\cdot$ with α-dicarbonyls such as ethyl pyruvate, 2,3-butanedione, and 2,3-pentanedione is proton abstraction from their enol tautomer. The rate-limiting step is first order for each reactant, the net products are enolate plus O_2 and H_2O_2, and the second-order rate constants (k) are the same, within experimental error, for the three substrates ($k = (4 \pm 1) \times 10^3\ \text{M}^{-1}\ \text{s}^{-1}$). For the reaction of benzil (an α-dicarbonyl that cannot enolize) with $O_2^{-}\cdot$ the rate-limiting step is first order for each reactant, and the second-order rate constant (k) is $(2 \pm 1) \times 10^3\ \text{M}^{-1}\ \text{s}^{-1}$. The process appears to involve an initial nucleophilic addition by $O_2^{-}\cdot$ to carbonyl carbon, followed by a dioxetane closure on the other carbonyl carbon and reductive cleavage by a second $O_2^{-}\cdot$ to give two benzoate ions and O_2.

Previous work has demonstrated that in aprotic media superoxide ion ($O_2^{-}\cdot$) adds nucleophilically to carbonyl carbons.[1-3] For those with adequate leaving groups (acid chlorides and carboxylate esters), the net reaction yields the carboxylate or peracid anions (eq 1). With acid

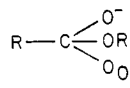


$$\begin{tikzcd}[column sep=small] RC(O)Cl + O_2^{-}\cdot \arrow[r, "k"] & RC(O)OO\cdot + Cl^{-} \arrow[r, "O_2^{-}\cdot"] \arrow[dl] & RC(O)OO^{-} + O_2 + Cl^{-} \\ \tfrac{1}{2}[\text{dimer}] \arrow[r, "-O_2"] & \tfrac{1}{2}[RC(O)OOC(O)R] \arrow[r, "O_2^{-}\cdot"] & RC(O)O^{-} + O_2 \end{tikzcd} \qquad (1)$$

chlorides the diacyl peroxide is a stable intermediate with limiting amounts of $O_2^{-}\cdot$ but is reduced by excess $O_2^{-}\cdot$ (eq 1 and 2).[1] In the case of esters the net rate depends on

$$RC(O)Cl + RC(O)OO^{-} \xrightarrow{-Cl^{-}} RC(O)OOC(O)R \xrightarrow{2O_2^{-}\cdot} 2RC(O)O^{-} + 2O_2 \quad (2)$$

the leaving group ($R'O^{-}$) of the activated complex I.[4]



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Thus, in pyridine the bimolecular rate constant, k_2, for the reaction of $O_2^{-}\cdot$ with ethyl acetate is $1.1 \times 10^{-2}\ \text{M}^{-1}\ \text{s}^{-1}$, and with phenyl acetate it is $160\ \text{M}^{-1}\ \text{s}^{-1}$. Because of the absence of a viable leaving group there is not a net reaction between $O_2^{-}\cdot$ and benzaldehyde. The same is true for

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