ration of solvent gave pale-yellow crystals (661 mg, 75.1%): mp 45–56 °C; IR ($CDCl_3$, NaCl) 1636 (C=C), 1424, 1214, and 1141 (OSO_2CF_3), 765 and 748 cm^{-1} (aryl); ^1H NMR ($CDCl_3$, internal Me_4Si) δ 5.16 (d, 1 H, C_9–H), 5.22 (s, 1 H, C_{10}–H), 6.81–6.97 (m, 1 H, C=C—H), 7.08–7.30 (m, 4 H, ArH), 7.36–7.63 (m, 4 H, ArH). Mass spectrum: electron impact, *m/z* 352 (12%, M^+), 220 (17%, $C_{16}H_{12}O$), 204 (35%, $C_{16}H_{12}$), 203 (22%, $C_{16}H_{11}$), 192 (58%, $C_{15}H_{12}$), 179 (100%, $C_{14}H_{11}$); chemical ionization, *m/z* 353 (29%, $M^+ + 1$), 352 (16%, M^+), 222 (100%, $C_{16}H_{14}O$), 221 (31%, $C_{16}H_{13}O$), 179 (44%, $C_{14}H_{11}$).

9,10-Dimethyl-9,10-ethenoanthracen-11-yl Triflate (3b). This ester was prepared from ketone **14b** (570 mg, 2.30 mmol) by following the same procedure as described for the preparation of triflate **3a**. It was obtained (669 mg, 76.6%) as light-yellow crystals: mp 118 °C, dec; IR ($CDCl_3$, NaCl) 1630 (C=C) 1408, 1220 and 1150 (OSO_2CF_3), 775 and 750 cm^{-1} (aryl); ^1H NMR ($CDCl_3$, internal Me_4Si) δ 1.96 (3 H, s, C_9–CH_3), 3.15 (3 H, s, C_{10}–CH_3), 5.97 (1 H, s, C=C—H), 7.22–8.09 (8 H, m, ArH). Mass spectrum: electron impact, *m/z* 380 (100% M^+), 232 (27% $C_{18}H_{16}$), 231 (88%, $C_{18}H_{15}$); chemical ionization, *m/z* 381 (23%, $M^+ + 1$), 380 (25% M^+), 232 (100%, $C_{18}H_{16}$).

Kinetic Studies. Ethanol was purified according to Wiberg.[18] Trifluoroethanol was purified according to Shiner et al.[19] or Rappoport.[20] Solvents were prepared by weight from conductivity water (Millipore Systems) and appropriate organic solvents. Conductivity measurements were performed in sealed, paired cells by using a Hewlett-Packard Model 4274 A LCR bridge, with 5.5 digit precision, interfaced with a Hewlett-Packard Model 3497 A multiplexer and a Hewlett-Packard Model 9826 BASIC microcomputer. From 1 to 10 μL (depending on concentration) of a pentane solution of the triflate was utilized (in-cell concentration of triflate was ca. 2×10^{-4} M) for each run. Approximately 200 points at equal changes in perecent reaction was collected over a range 5–95% reaction. Rate constants were calculated by using a BASIC version nonlinear least-squares program written for the HP 9826 in our laboratories. Temperature control and measurement were accomplished by using a PRT-regulated proportional temperature controller and Hewlett-Packard quartz thermometer.

Product Study. Triflate **3b** was solvolyzed in 70% v/v EtOH at 85 °C for at least 10 half-lives. The capillary GLC analysis of the crude mixture showed only one product which was identical in IR with the authentic sample of ketone **14b**.

Acknowledgment. This investigation was supported by the National Cancer Institute (CA 16903-06) of the National Institute of Health at Utah. The purchase of the rate acquisition instrumentation at William and Mary was made possible by the NSF 2- and 4-year College Research Equipment Program.

Registry No. 3a, 91759-14-7; **3b**, 91759-15-8; **14a**, 6372-63-0; **14b**, 73164-06-4.

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Thermochemistry of *trans*-Di-*tert*-butyl Hyponitrite

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Abstract: The heat of combustion of *trans*-di-*tert*-butyl hyponitrite, $\Delta H_{comb} = 1304.5 \pm 1.8$ kcal/mol, and its heat of vaporization, $\Delta H_v = 17.7 \pm 0.3$ kcal/mol, determined by an effusion technique, were used to calculate $\Delta H_f^\circ = -41.3 \pm 2.9$ kcal/mol. This represents the first experimental determination of a heat of formation of a hyponitrite. From additivity relationships we estimate ΔH_f°(*trans*-HON=NOH) = 3.1 ± 3.1 kcal/mol, in good agreement with two reported values obtained by MO methods. The activation energies for homolysis of a number of *trans*-hyponitrites were estimated from additivity relationships, but did not agree well with experimental values. This result is associated with a compensating, linear relation between E_a and log A in the hyponitrite series.

The use of azo compounds for generation of radicals and biradicals has received an enormous amount of attention for theoretical[1a] and practical[1b] reasons, the bulk of which has focused on azoalkanes.[1a] We have elsewhere described the spectroscopy,[2a] kinetics,[2b] and excited-state yields[2c] from a number of *trans*-hyponitrites. In this paper we present the first experimental data on the heat of formation of an alkyl hyponitrite and derive relations between the thermochemistry and activation parameters of a series of these compounds.

Experimental Section

A sample of *trans*-di-*tert*-butyl hyponitrite was prepared[3] and recrystallized from CH_2Cl_2–CH_3OH at low temperature. The same batch of crystals was used for combustion and effusion measurements. The purity of the material was established from the melting point (84.5 °C dec; lit.[4] 84–84.5 °C dec) and UV spectrum (λ_{max} 223.4 nm (ϵ 7140 M^{-1} cm^{-1}) in pentane; lit.[5] λ_{max} 223.4 nm (ϵ 7130 M^{-1} cm^{-1})). **Caution**: The substance can detonate if struck.

Table I. Combustion Data for Di-*tert*-butyl Hyponitrite

wt, g	ΔT, °C	HNO_3 correction, cal	fuse correction, cal	$\Delta H_{combustion}{}^{298}$ cal/g	$\Delta H_{combustion}{}^{298}$ kcal/mol
0.28942	0.980	9.55	11.5	7510.01	1306.74
0.36789	1.152	14.00	17.6	7482.49	1301.95
0.28620	0.892	10.80	0	7492.58	1303.71
0.38140	1.190	14.20	0.5	7502.70	1305.47
0.30811	0.960	10.30	0	7497.39	1304.55

p-Bromochlorobenzene (Aldrich) was recrystallized from dichloromethane: mp 66.5–67 °C (lit.[6] 68 °C); λ_{max} 224.2 nm in isooctane (ϵ 1.26×10^4 M^{-1} cm^{-1}).

The heat of combustion of solid DBH was determined with a constant volume Parr Model 1241 adiabatic bomb calorimeter, standardized with

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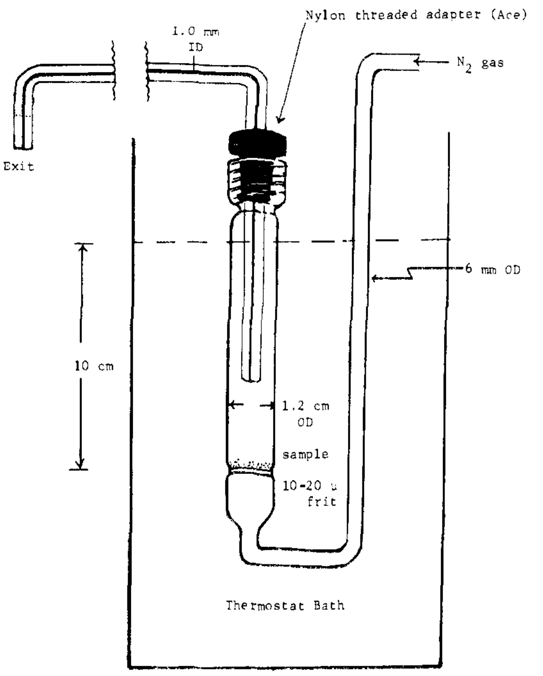

Figure 1. Schematic of apparatus for effusion study.

NBS 39i grade benzoic acid (heat of combustion = 6318 cal/g). The energy equivalent of the apparatus was determined as 2417.0 ± 4.3 cal/°C. The sample size was restricted to 0.4 g or less because of the violence of combustion.

The apparatus for the effusion measurements is shown in Figure 1. The sample (0.2–0.4 g) was placed in an even layer on the frit, and the assembled apparatus was immersed in a thermostated bath (Neslab Model EX-500) held to ±0.1 °C. A steady flow of N_2 (48 mL/min) was maintained for 30 min before starting a collection by immersing the tip of the capillary tubing vertically to a fixed depth (ca. 1 cm) into 10 mL of isooctane (spectrophotometric grade). Control experiments indicated that the N_2 stream was saturated with sample vapor at the chosen flow rate and that the final absorbance readings remained constant on the time scale of the experiment.

Results

The results of the calorimetric measurements are given in Table I. The mean of the five corrected heats of combustion was 1304.5 ± 1.8 kcal/mol. Taking into account the error in the energy equivalent for the apparatus, we calculate $\Delta H_{\mathrm{f,solid}} = -59.0 \pm 2.9$ kcal/mol.

The results of the effusion measurements on hyponitrite are presented as plots of absorbance at $\lambda_{\max}$ vs. time in Figure 2. Analysis by the method of least squares gave values of the slopes with $r > 0.998$ in every case. A semilogarithmic plot of slope vs. T^{-1} (Figure 3) was reasonably linear and gave a value of $\Delta H_{\mathrm{vap}} = 17.7 \pm 0.3$ kcal/mol ($r = 0.9988$) with neglect of the point at the highest temperature. This result is slightly higher than a reported[5] value of 15.7 kcal/mol. The effusion technique was checked with *p*-bromochlorobenzene, which gave a similar result (deviation of point at 25.3 °C) and $\Delta H^{\circ}_{\mathrm{vap}} = 15.9 \pm 0.4$ kcal/mol (four points, −0.3 to 19 °C). This compared well with a reported value[7] of 16.7 kcal/mol obtained at higher temperatures. With *p*-bromochlorobenzene we also calculated the vapor pressure, under the assumption of quantitative trapping, from the equation $\mathrm{d(absorbance)}/\mathrm{d}t = \epsilon f p_{\mathrm{vap}}/RTV$, where f is the flow rate, T is the ambient temperature, and the other symbols have their conventional meanings. At 19.0 °C we obtained a value of 0.13 torr, compared with calculated pressure of 0.14 torr from a published equation[7] valid over the temperature range 23.0–63.0 °C.

Combining our experimental heat of vaporization with the heat of formation of solid *tert*-butyl hyponitrite leads to $\Delta H_f^{\circ} = -41.3 \pm 2.9$ kcal/mol.

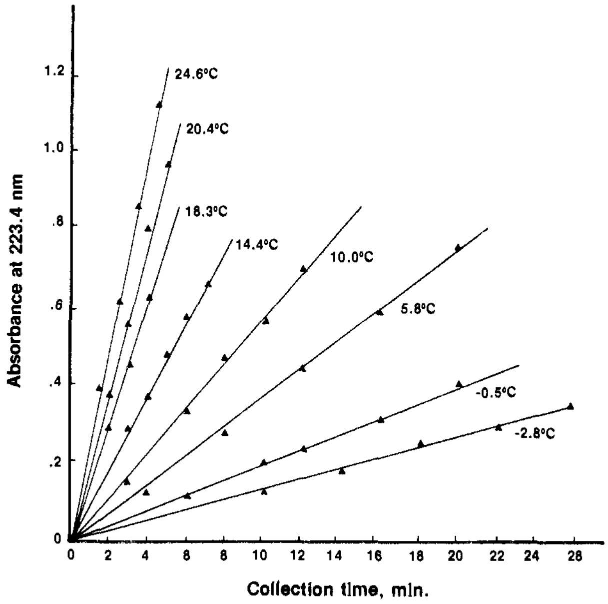

Figure 2. Absorbance from di-*tert*-butyl hyponitrite in isooctane as a function of collection time.

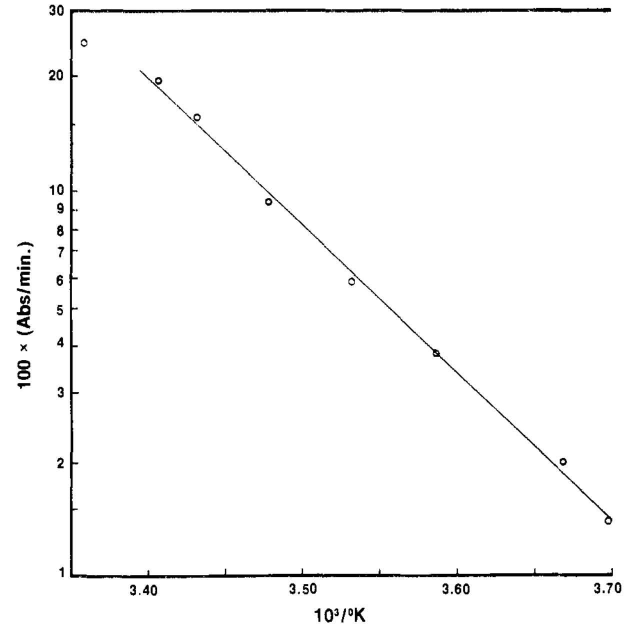

Figure 3. Semilogarithmic plot of slopes from Figure 2 vs. reciprocal temperature.

Discussion

Experimental Data. The precision of the heat of combustion we obtained for the hyponitrite is less than usual because of the smaller sample sizes involved and consequently smaller temperature increases after ignition. Even with the reduced amounts of sample, the metal cup was often dislodged from its retaining ring on ignition, and in two cases the combustion was so facile that the fuse wire was severed but did not ignite (Table I).

Our effusion apparatus partly avoids the problems of surface absorption that make correction factors necessary with direct optical methods.[5] The trapping of the sample vapor into the isooctane appeared to be fairly efficient from the results with the test compound, in spite of the simplicity of the apparatus. For the purposes of obtaining ΔH_{vap} it is only necessary that a constant fraction of the vaporized sample is trapped by the liquid, however, and this assumption appears to be valid in our system except at temperatures above 20 °C. At extended collection times we would expect curvature of plots in Figure 2 due to saturation of the liquid. The highest concentrations obtained with the hyponitrite in the

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(7) "C. R. C. Handbook of Chemistry and Physics", 60th ed.; CRC Press: Boca Raton, FL, 1979–80; p D-219.

collection flask were $<2 \times 10^{-4}$ M, which is far below the saturated level and consistent with the linearity of the plots. We felt justified in omitting data obtained above 20 °C because at such temperatures crystals appeared on the inner walls of the capillary tubing near the collector exit.

The use of the same batch of sample for measurement of both heat of vaporization and heat of combustion avoids to an extent errors due to differences in crystalline form or the presence of minor impurities, since a change in the forces binding the molecules in the solid should affect the two determinations in compensating ways.

Analysis by Group Contributions and Relation to Hyponitrous Acid. Although no thermodynamic data on hyponitrites appear to be available, there are two reported calculations on the corresponding hyponitrous acid (*trans*-HO—N=N—OH) of −0.5[8] and 3.6[9] kcal/mol. The difference

$$\Delta H_f^\circ(t\text{-BuON=NOBu-}t) - \Delta H_f^\circ(\text{HON=NOH}) = (-41.3 \pm 2.9) - (1.6 \pm 2.0)^{8,9} = -42.9 \pm 3.5\ \text{kcal/mol} \tag{1}$$

is, within error, equal to twice the difference

$$\Delta H_f^\circ(t\text{-BuON=O}) - \Delta H_f^\circ(\text{HON=O}) = (-41.0 \pm 1)^{10} - (-18.8 \pm 0.3)^{11} = -22.2 \pm 1.0\ \text{kcal/mol} \tag{2}$$

This result gives us some confidence in our experimental determination.

We assign group values[12] for di-*tert*-butyl hyponitrite as follows (N_a = (N=N)):

$$\Delta H_f^\circ(trans\text{-}t\text{-Bu}_2\text{N}_2\text{O}_2) = 6[\text{C}-(\text{H})_3(\text{C})] + 2[\text{C}-(\text{O})(\text{C})_3] + 2[\text{O}-(\text{N}_a)(\text{C})] + 2[(\text{N}_a)-(\text{O})] + 4\ \text{gauche interactions} \tag{3}$$

From the results of eq 1 and 2, we may assign $[\text{O}-(\text{N}_a)(\text{C})] = [\text{O}-(\text{N=O})(\text{C})] = -5.9$ kcal/mol. Assigning other known values,[12] we obtain

$$-41.3 = 6(-10.08) + 2(-6.6) + 2(-5.9) + 2[(\text{N}_a)-(\text{O})] + 4(0.8) \tag{4}$$

This gives $[(\text{N}_a)-(\text{O})] = 20.5$ kcal/mol.

A value of $\Delta H_f^\circ(trans\text{-H}_2\text{N}_2\text{O}_2) = 3.1$ kcal/mol is obtained from the difference in eq 2 applied to our experimental heat of formation. With this value we have

$$\Delta H_f^\circ(trans\text{-H}_2\text{N}_2\text{O}_2) = 2[\text{O}-(\text{H})(\text{N}_a)] + 2[(\text{N}_a)-(\text{O})] \tag{5}$$

or

$$3.1 = 2[\text{O}-(\text{H})(\text{N}_a)] + 2(20.5)$$

This leads to the group value $[\text{O}-(\text{H})(\text{N}_a)] = -19.0$ kcal/mol.

Relation to Activation Parameters for Homolysis. The thermolysis of di-*tert*-butyl hyponitrite has been suggested to proceed through a concerted process on the basis of a small activation volume.[13] If, on the other hand, we assume a stepwise decomposition, we have

$$\underset{\Delta H_f^\circ = -41.3}{t\text{-BuO—N=N—OBu-}t} \quad \underset{E_{-\text{DBH}}}{\overset{E_{\text{DBH}}}{\rightleftharpoons}} \quad \underset{-23.8^{14}}{t\text{-BuO}\cdot} + \underset{\text{DTO}}{\cdot\text{N=N—OBu-}t} \tag{6}$$

From experimental activation energies of 28.6[4] and 30.1[5] kcal/mol and on the assumption $E_{-\text{DBH}}$ is negligible, we calculate a mean value of $\Delta H_f^\circ(\text{DTO}) = 11.9$ kcal/mol. The group contributions for this radical are

$$\Delta H_f^\circ(\text{DTO}) = 3[\text{C}-(\text{H})_3(\text{C})] + [\text{C}-(\text{O})(\text{C})_3] + [\text{O}-(\text{C})(\text{N}_a\cdot)] + 2\ \text{gauche interactions} \tag{7}$$

Substituting known and derived values from above, we obtain $[\text{O}-(\text{C})(\text{N}_a\cdot)] = 11.9 - 3(-10.08) - (-6.6) - 2(0.8) = 47.1$ kcal/mol. This radical group contribution and the ones for the hyponitrite allow us to calculate heats of formation and activation energies for a number of simple hyponitrites. In general terms for the reaction

$$\text{R}_3\text{CON=NOCR}_3 \rightarrow \text{R}_3\text{CO}\cdot + \cdot\text{N=NOCR}_3 \tag{8}$$

(R = H or alkyl separately)

we have the additivity relations

$$\Delta H_r(8) = \Delta H_f^\circ(\cdot\text{N=NOCR}_3) + \Delta H_f^\circ(\text{R}_3\text{CO}\cdot) - \Delta H_f^\circ(\text{R}_3\text{CON=NOCR}_3)$$

$$= [\text{C}-(\text{R})_3(\text{O}\cdot)] + [\text{C}-(\text{R})_3(\text{O})] + [\text{O}-(\text{C})(\text{N}_a\cdot)] - 2[\text{C}-(\text{R})_3(\text{O})] - 2[\text{O}-(\text{C})(\text{N}_a)] - 2[\text{N}_a-(\text{O})] + \text{gauche corrections}$$

Reducing the terms through substitution we obtain

$$\Delta H_r = 17.9 + [\text{C}-(\text{R})_3(\text{O}\cdot)] - [\text{C}-(\text{R})_3(\text{O})] + \text{gauche corrections}$$

Table II. Calculation of Heats of Homolytic Dissociation (in kcal/mol) from Additivity

R in $R_2N_2O_2$	$[C-(R)_3(O\cdot)]$[a]	$[C-(R)_3(O)]$[b]	gc[c]	ΔH (8)	E_{obsd}
CH_3	1.94	−10.08	0	29.9	25.4[d]
CH_3CH_2	4.9	−8.1	0	30.9	27.2[d]
$(CH_3)_2CH$	6.0	−7.0	−0.8	30.1	26.8[d]
$(CH_2)_5CH$	6.0	−7.0	−0.8	30.1	27.3,[d] 28.4[e]
$(CH_3)_3C$	6.6	−6.6	−1.6	29.5	28.6,[f] 30.1[g]
$CH_3CH_2C(CH_3)_2$	6.6	−6.6	−1.6	29.5	27.6[h]

[a] Group values calculated from those for corresponding alcohol with assumption of ΔH_D°(RO–H) = 103 kcal/mol, except for ΔH_D°(CH_3O–H) = 102 kcal/mol.[18] [b] Values from ref 12. [c] Gauche corrections. [d] In *tert*-butylbenzene (Quinga, E. M. Y.; Mendenhall, G. D., unpublished work). [e] Calculated from data in ref 19. [f] Calculated from data in ref 4. [g] Calculated from data in ref 5. [h] In isooctane, determined by HPLC by M. Dziobak.

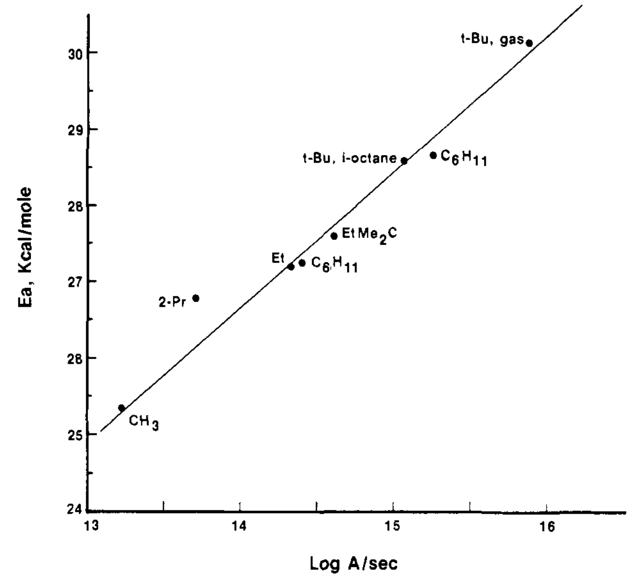

Figure 4. Activation energies vs. log *A* for aliphatic hyponitrites, from Table II.

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(13) Neumann, R. C., Jr.; Bussey, R. J. *J. Am. Chem. Soc.* **1970**, *92*, 2440–5.

(14) (a) Calculated from ΔH_f°(*t*-BuOH) = −74.72 ± 0.21 kcal/mol[14b] and ΔH°_D(*t*-BuO–H) = 103 kcal/mol. (b) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970.

The group terms and calculated values of ΔH_r for reaction 8 for methyl and primary, secondary, and tertiary alkyl hyponitrites are given in Table II. This approach leads to prediction of rather uniform heats of dissociation, which do not agree with the experimental values except for *tert*-butyl hyponitrite, from which they were derived.

The apparent reason for this failure is seen when the hyponitrite activation energies (gas phase or in hydrocarbon solvents) are plotted against the respective values of log A (Figure 4). Since $\log A = \log (ekT_m/h) + \Delta S^\ddagger/2.3R$ and $E_a = \Delta H^\ddagger + RT_m$, this plot is an example of a familiar relation of the type $\Delta H^\ddagger = \beta\Delta S^\ddagger + \text{constant}$.[15] The slope of our plot is $2.3R\beta$, from which we obtain an isokinetic temperature $\beta = 357$ K. The extrapolated rate constants at this temperature (84 °C) from the eight examples in fact showed a narrow range of 0.0026–0.0053 s^{-1}.

The relationship in Figure 4 is analogous to ones involving medium and substituent effects on decomposition rates of phenylazotriphenylmethanes,[16] for which there is rather good evidence for a one-bond scission process.[17] Aside from illustrating a possible mechanistic continuity, however, the relationship does not provide evidence for the nature of the mechanism itself. Our result does partly supercede an earlier attempt[2b] to correlate faster decomposition rates (isooctane, 66 °C) with increasing inductive effects in the alkyl group, since any ordering of the aliphatic alkyls may be reversed above the isokinetic temperature.

Our assumption of a one-bond scission process for homolysis of the hyponitrite can be reconciled with a two-bond concerted scission advocated from other evidence,[13] if we assume that loss of the nitrogen from the RO—N=N· radical is competitive with escape from the solvent cage. This should be true if the rate constant for this loss is on the order of 10^{12} s^{-1}, which will be the case if the reaction has a preexponential factor that is usual for first-order scission reactions ($>10^{13.5}$ s^{-1}) and an activation energy of less than 1 kcal/mol. These assumptions may be reasonable, since our calculations show the reaction in question to be exothermic by about 30 kcal/mol.

Conclusions

The gas-phase heat of formation of di-*tert*-butyl hyponitrite has been determined as −41.3 ± 2.9 kcal/mol. This value together with available kinetic data has allowed us to estimate enthalpy group equivalents for $[O-(N_a)(C)_a] = -5.9$ kcal/mol, $[N_a-(O)] = 20.5$ kcal/mol, and $[N_a-(O\cdot)] = 47.1$ kcal/mol, with the last value derived under the assumption of single N–O bond scission. These equivalents do not correctly predict activation energies of other aliphatic hyponitrites, due to the variability of E_a according to the isokinetic equation E_a (kcal/mol) = (1.63 ± 0.09) log (A/s^{-1}) + (3.87 ± 1.35).

Note Added in Proof. Although a weak isokinetic relationship exists in the series shown in Figure 4, the plot itself is not statistically significant.[20] The individual Arrhenius plots for the compounds in fact do not intersect at the isokinetic temperature derived from the figure.

Acknowledgment. This work was supported in part by the U.S. Army Research Office.

Registry No. *trans*-$((CH_3)_3C)_2N_2O_2$, 82554-97-0; $H_2N_2O_2$, 14448-38-5; *trans*-$(CH_3)_2N_2O_2$, 86886-15-9; *trans*-$(CH_3CH_2)_2N_2O_2$, 91606-80-3; *trans*-$((CH_3)_2CH)_2N_2O_2$, 86886-16-0; *trans*-$((CH_2)_5CH)_2N_2O_2$, 86886-18-2; *trans*-$(CH_3CH_2C(CH_3)_2)_2N_2O_2$, 85972-35-6; *trans*-$H_2N_2O_2$, 19467-31-3.

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