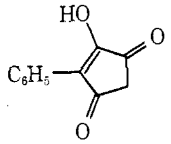
much of the stabilization of the oxocarbon dianions is due to energetic and how much to entropy effects? Unfortunately, for the crucial second step of ionization, no data at different temperatures are available for any of the oxocarbons.

Turning now to substituted oxocarbons, the addition of a substitutent group which breaks the symmetry should partially localize charge and hence reduce stabilization of the oxocarbon anions, relative to reference species. Enols of 1,3-diketones, which can be taken as reference compounds, usually have pK = 4.5–5.5. The substituted oxocarbons **1** and **3** have pK values near 2 (Table I); the modest increase in acidity of 3 pK units can perhaps be associated with cyclodelocalization in anions of these species. A still better reference compound for **3** is **5**, for which Yamazaki reports pK = 3.55,[13] or about 2 pK units greater than for **3**.

The four-membered ring compounds **2** and **4** show still higher acid strength. This finding is paralleled by the fact that enols of 1,3-diketones in four-membered rings generally show enhanced acidity. For example, cyclobutane-1,3-dione shows pK = 3.0 compared to 5.25 for 1,3-cyclohexanedione. Smutney, Caserio, and Roberts[12] have discussed the high acid strength of **2**; they suggest that 1,3-transannular bonding as in resonance structure **6** may be responsible, and support this suggestion with qualitative MO calculations.[12] However, Johns and Kriegler[16] have pointed out that favorable dipolar interaction between the CO groups can account for most of the increased acid strength of four-ring 1,3-dicarbonyl compounds. Entropic effects of the sort found by Schwartz and Howard may also be important.[15] Whatever the source of the enhanced acidity of four-membered ring compounds of this type, it is apparently reflected in the acid strength of **2** and **4**, where it combines with electron delocalization to make these compounds very strong acids indeed.[17]



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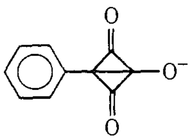

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It is interesting that the enhanced acidity of four-ring dicarbonyl compounds is not found for squaric acid itself, which is actually somewhat weaker in its second dissociation constant than the five-membered ring croconic acid. The stability of squarate dianion may be reduced by 1,3-transannular electron repulsion interactions between carbon atoms, as suggested also by detailed vibrational analysis of the dianion.[3]

Acknowledgment. This work was partially supported by a grant from the National Science Foundation.

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[16] R. B. Johns and A. B. Kriegler, *Aust. J. Chem.*, **17**, 765 (1964).

[17] Dissociation constants of two substituted phenylhydroxycyclobutenediones have been measured by W. Broser and M. Seekamp [*Tetrahedron Lett.*, **51**, 6337 (1966)]. They report pK = 1.85 for *p*-methoxyphenylhydroxycyclobutenedione and pK = 2.05 for *p*-hydroxyphenylhydroxycyclobutenedione; their values are repeated in a recent review.[18] These data were obtained potentiometrically on 10^{-2} solutions in 50% aqueous acetone. It is likely that this method gives inaccurate results at this concentration and that Broser and Seekamp's results are in error.

[18] W. Reid and A. H. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **11**, 997 (1972).

N-tert-Butylanilino Radicals. II. Dimerization of *N*,3,5-Tri-*tert*-butylanilino Radicals

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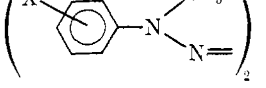
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received July 28, 1973*

Abstract: Thermodynamic parameters for the reaction $(ArN\text{-}t\text{-}Bu)_2 \rightleftarrows 2(ArN\text{-}t\text{-}Bu)$, $K = k_1$ (forward reaction)/k_2 (reverse reaction), have been evaluated to be $K = \exp(-31{,}200/RT)\exp(73/R)$, and $k_2 = kt/h \exp(+2200/RT)\exp(-65/R)$ by measuring the concentration of ArN-*t*-Bu using esr. The implications of these unusual $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for the mechanism of the reaction are discussed, and it is concluded that their unusual sizes are dictated by the severe conformational restraints on the reaction.

In a previous paper on *N-tert*-butylanilino radicals,[1] it was found that both electron-withdrawing and -releasing substituents at the para position of the benzene ring decrease the nitrogen esr splitting constant (a(N)), demonstrating that these radicals are members of Walter's "class S,"[2] in which both types of substituents affect properties such as a(N) in the same direction. This was of particular interest with regard to the effect of substituent upon the rate of decomposition of 1,4-dimethyl-2-tetrazenes (**1**). Since **1** (4-OCH_3) decomposed 200 times as fast as **1** (4-CO_2Et), and other substituents followed the Hammett equation reasonably



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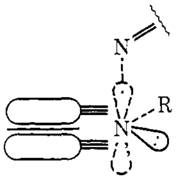

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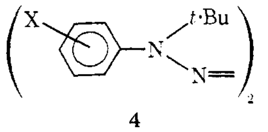

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[1] S. F. Nelsen, R. T. Landis, L. H. Kiehle, and T. H. Leung, *J. Amer. Chem. Soc.*, **94**, 1610 (1972).

[2] (a) R. I. Walter, *ibid.*, **88**, 1923 (1966). (b) For a review of Hammett behavior of esr splittings, see E. G. Janzen, *Accounts Chem. Res.*, 2, 279 (1969).

Table I. Rate Constants for Gas Evolution from 1,4-Di-*tert*-butyl-1,4-diaryl-2-tetrazenes (**4**)

Compd	Source	Temp, °C	10^4K, sec^{-1}	Rel rate, 90°	ΔH, kcal/mol	ΔS, eu
4 (X = 4-OCH$_3$)	*a*	65.9	0.265, 0.267	4.48	29.4	+7.5
	a	74.1	1.36, 1.40			
	b	80.0	1.74, 1.75, 1.76			
	a	81.0	2.66, 2.71, 2.63			
	a	88.1	4.51, 4.66, 4.63			
	a	96.8	14.3, 13.8, 14.0			
4 (X = H)	*b*	79.9	0.428, 0.434, 0.426	1	25.6	−6.0
	a	81.0	0.493, 0.512, 0.514			
	a	89.4	1.22, 1.22, 1.23			
	a	97.4	3.22, 3.36, 3.26			
	b	98.9	3.80, 3.76, 3.78			
	a	105.3	7.47, 7.56, 7.34			
	a	111.8	10.21, 10.11, 10.12			
	a	117.7	14.48, 14.23, 14.30			
4 (X = 4-CN)	*b*	79.8	0.595, 0.594, 0.600	1.06	25.3	−6.8
	b	89.7	1.18, 1.13, 1.18, 1.17			
	b	98.9	3.43, 3.39, 3.47			
	b	107.6	8.44, 8.51, 8.41			

[a] Determined by L. H. Kiehle,[1] but using calculated end point. [b] Determined by R. T. Landis, II, this work, calculated end point.

well[3] ("class O" behavior in Walter's classification), the effectiveness of the aryl group in delocalization of the odd electron from the anilino nitrogen was not the principal factor in controlling decomposition rate of the 2-tetrazenes **1**. We suggested that the cause of the rate-slowing effect of electron-withdrawing substituents, which showed up mainly in the $\Delta S^{\ddagger}$ term for **1** decomposition rates, was attributable to a conformational change which is necessary to allow decomposition of **1**. The ground-state conformation of **1** should resemble **2**, in which the "lone pair" of the anilino nitrogen is sterically arranged for maximum delocation into the benzene ring. The geometry of **2** is very poor for decomposition, however, since stretching the N_1–N_2 bond would form an approximately sp^2-hybridized radical which would be perpendicular to the aryl MO's, and not result in stabilization. We argued[1,3] that a conformation like **3**, allowing maximum stabilization of the odd-electron MO forming at the anilino nitrogen by the aryl group, must be attained. This idea was substantiated by the greatly decreased substituent effect on decomposition rate for **4** relative to **1**: k (X = 4-OCH$_3$)/k (X = H) was 24 at 110° for **1**,[3] and only 5.5 at 81° for **4**. Since replacement of the *N*-methyl group of **1** by the *tert*-butyl group in going to **4** would destabilize conformation **2** and twist the aryl ring out of conformation with the "lone pair" orbital at the anilino nitrogen, one would expect a less important substituent effect. We report here some additional data which further substantiate the conformational change argument.

We also suggested that conformational effects ought to be important in dimerization of arylamino radicals, and that studies such as those of Wieland[4] on hydrazine radical equilibria may well not be closely related to the effects of odd-electron delocalization. In this paper we report studies on the hydrazine–amino radical equilibrium of *N*,3,5-tri-*tert*-butylanilino radicals, which show the great dominance of entropy terms over enthalpy terms in the dimerization reaction.

Results

Rates of Tetrazene Decomposition. We have completed more experiments on decomposition rates of **4**, measuring the change in pressure caused by gas evolution, using the constant-volume apparatus employed in the previous work.[1,3] We decided that a major source of the scatter previously observed[1] for **4** (X = H) and **4** (X = 4-OCH$_3$) rates was instability in the pressure transducer-recorder system while awaiting complete decomposition. In analyzing the data quoted in ref 1, we employed the pressure observed after 8–10 half-lives for decomposition as P_∞, but we have now recalculated rate constants from these data, adjusting P_∞ to give minimum least-squares deviation from linearity in the first-order plots, and quote these rate constants in Table I. Comparison with our previously reported rate constants will show that scatter is considerably decreased. After redetermination of a few runs on the previous compounds to assure us that the data would be consistent, R. T. L. also ran kinetics on **4** (X = 4-CN), and the results also appear in Table I. The comparison of rates at 90° shows that the rate of decomposition of **4** is far less sensitive to substituent than is that of **1**, and that **4** (X = 4-CN) decomposes at virtually the same rate as that of **4** (X = H). Because of the very small substituent effect on the decomposition rates of **4**, and the possibility that some conformational effects are still appearing in the measured rates,[5] we did not believe that more extensive rates studies were worth pursuing.

In another minor addition to the earlier work, we prepared **4** (X = 3-OCH$_3$) and **4** (X = 3-Cl) to see how a(N) for the meta-substituted compounds would correlate with those for the para-substituted ones.[6] Unfortunately, we never were able to obtain the esr spectrum of the anilino radical from **4** (X = 3-Cl) in a number of attempts. We observed that from **4** (X = 3-OCH$_3$), and found a(N) = 9.60, a(H$_o$) = 6.52, 5.14,

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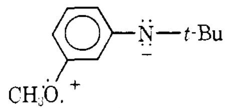
(3) S. F. Nelsen and D. H. Heath, *J. Amer. Chem. Soc.*, **91**, 6452 (1969).

(4) For a review of diarylamino radical chemistry, see A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y., 1968, pp 111–136.

(5) It may be noted that **4** (4-OCH$_3$C$_6$H$_4$) decomposes more rapidly than **4** (4-CNC$_6$H$_4$), despite the fact that cyanophenyl is more effective at decreasing spin density at the anilino nitrogen than is methoxyphenyl, as judged by a(N) values.[1] There are undoubtably several rationalizations conceivable for this small effect; we prefer not to speculate.

(6) We presume there is at least some interest in this point, since the referees of the earlier paper requested some meta substituents.

$a(H_p) = 7.46$, $a(H_m) = 2.01$ (2 H) G. We believe it worth noting that the methoxyl methyl splitting was not resolved ($a(OCH_3) < 0.1$ G), although $a(OCH_3)$ was 0.91 G for the 4-methoxy compound. Similarly, a(N) was decreased far less by 3-methoxy than by 4-methoxy substitution (0.1 *vs.* 0.3 G). The reason for this difference in effect of the 3- and 4-substituted compounds is not apparent in the simplest resonance structure type of rationalization, since if anything, **5** might be slightly preferred over **6** due to marginally less change separation; meta substituents are not "insulated" from single electron donation to a benzylic radical center in the same sense as they are from two electron donation to a benzylic cation center. The origin of the clear-cut difference lies in the substantially lower spin density at the 3 position compared to the 4 position (the 3 position lies at a Hückel node for spin density, and a (−) 3.6 ratio of $a(H_p)/a(H_m)$ was observed for *N-tert*-butylanilino radical). The nitrogen splittings for 3-methoxy-*N-tert*-butyl- and *N*,3,5-*tert*-butylanilino radicals have been added to those from ref 1 in Figure 1; the trend is not affected very much.



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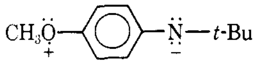

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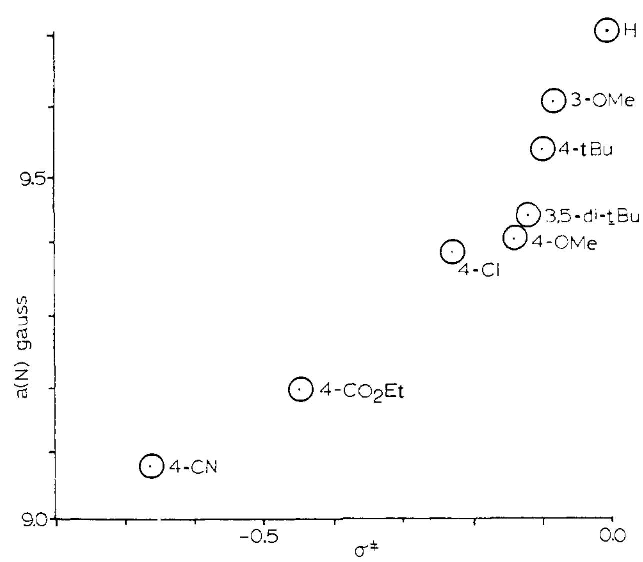
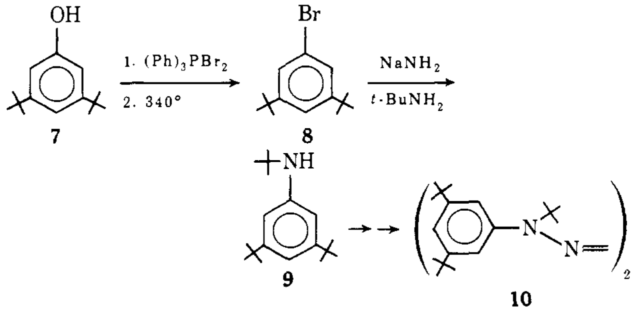
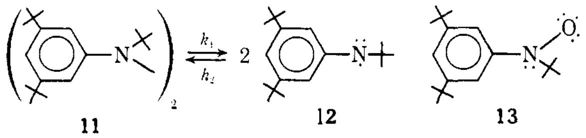


Figure 1. Plot of a(N) *vs.* substituent $\sigma^{\ddagger}$ value ($\sigma^{\ddagger} = -\sigma$ for $\sigma > 0$, $\sigma^{\ddagger} = \sigma/2$ for $\sigma < 0$) for substituted *N-tert*-butylanilino radicals.

Scheme I. Synthesis of 1,4-Di-*tert*-butyl-1,4-bis(3′,5′-di-*tert*-butylphenyl)-2-tetrazene



Hydrazine–Amino Radical Equilibrium. To extend kinetic studies to the hydrazine–amino radical equilibrium, we needed a clean example of such an equilibrium. As might have been expected from product studies on diarylamino radicals published by the groups of Neugebauer[7] and Bridger,[8] the final products of decompositions of the **4** molecules discussed above are complex, and involve a variety of C–N and C–C bond formations, with subsequent oxidation to aromatic amines. We were unable to detect the hydrazine in the decomposition of **4** (X = 4-*tert*-butyl), and also failed to isolate the hydrazine by oxidations of the amine with silver oxide, potassium permanganate, potassium ferrocyamide, or lead tetraacetate, reagents which are successful in preparing tetraarylhydrazines from diarylamines. It had already been established that even the N–H substituted 2,4,6-tri-*tert*-butylanilino radical does not dimerize efficiently,[9] and yet we needed the *N-tert*-butyl group to prevent rapid disproportionation at the *N*-alkyl group.[3] We therefore decided to try blocking formation of bonds to both ortho and para ring positions by 3,5-di-*tert*-butyl substitution. The required aniline (**9**) was prepared from 3,5-di-*tert*-butylphenol (**7**) by conversion to the bromide (**8**) and benzyne formation in the presence of *tert*-butylamine (Scheme I). Compound **9** was converted to the tetrazine (**10**) by the standard sequence of N-nitrosation, reduction to the hydrazine, and oxidation with quinone. Thermal decomposition of **10** gave a compound subsequently identified as the related hydrazine **11**, without observation of the complex mixtures of products derived from C–N and C–C bond formation, and aromatization. This compound was less tediously prepared by mixing the *N*-chloroaniline (from **9** and calcium hypochlorite[10]) with the *N*-lithioaniline (from **9** and *n*-butyllithium) at −78°, and isolation by tlc. The product had no N–H absorption in the ir, the correct high resolution mass spectrum parent peak for a dimer, and an nmr spectrum of the proper symmetry for **11**. Heating or photolyzing either **10** or **11** gave the esr spectrum of *N*,3,5-tri-*tert*-butylanilino radical **12**, $a(N) = 9.44$, $a(H_o) = 5.65$ (2 H), $a(H_p) = 7.13$, $g = 2.0033$. If the samples were not degassed, the esr spectrum of the related nitroxide **13** was observed; $a(N) = 12.07$, $a(H_o, H_p) = 2.04$ (3 H), $g = 2.006$ in heptane, −40°. Our initial attempts at quantitative measurements on the rate disappearance of **12** from irradiated samples of **11** were frustrated by appearance of **13** when the concentration of **12** had fallen to low values, in spite of the fact that **13** was not discernible at high concentrations of **12**. We attribute this behavior to introduction of enough oxygen in manipulation of the samples of **11** to form some **13**, which forms mixed



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(7) F. A. Neugebauer and S. Bamberger, *Angew. Chem., Int. Ed. Engl.*, **10**, 71 (1971).

(8) R. F. Bridger, *J. Amer. Chem. Soc.*, **94**, 3124 (1972).

(9) E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2027 (1963); *J. Chem. Soc.*, 3540 (1961).

(10) For isolation of *N*-chloro-*N-tert*-butylaniline, see P. G. Gassman and G. A. Campbell, *J. Amer. Chem. Soc.*, **93**, 2567 (1971).

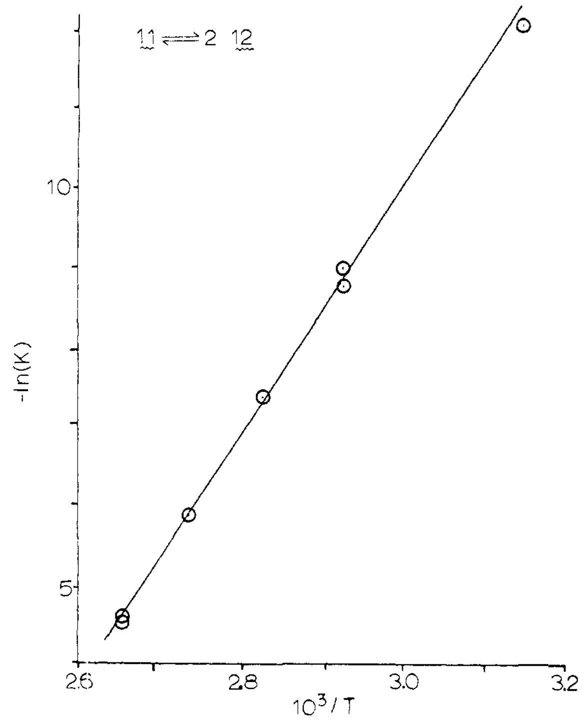


Figure 2. Plot of $-\ln K$ *vs.* $10^3/T$ for the data (Table II) on the hydrazine–amino radical equilibrium.

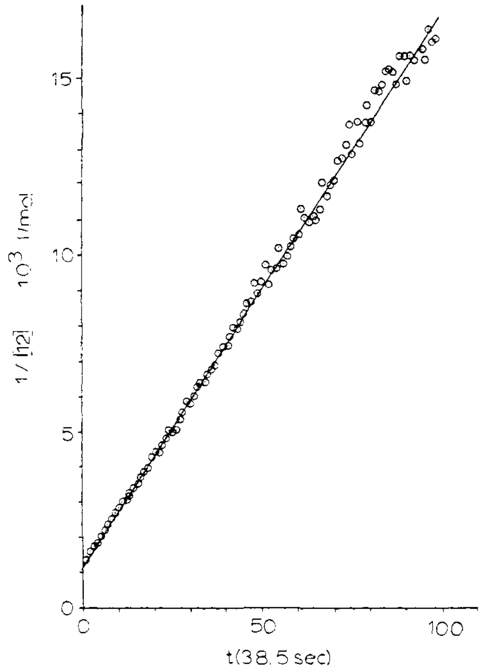
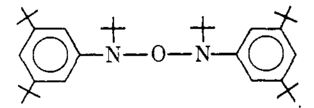


Figure 3. Second-order plot for disappearance of the esr signal of the amino radical **12** at $-66.8°$. The slope of the least-squares line gives $k_3 = 4.11$ l./(mol sec).

dimers with **12**, and so is not detected by esr. We write the mixed dimer of **12** and **13** as **14**, mainly for



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convenience, but also by analogy with the early observations of Wieland[11] that oxygen transfer takes place between diaryl nitroxides and tetraarylhydrazines upon heating. If **13** reacted substantially more rapidly with **12** than did a second molecule of **12**, and the average rates of **11** and **14** cleavage were fairly comparable, one would not be able to observe the nitroxide **13** until the concentration of amino radicals **12** had fallen to a low value, which is consistent with our observation. We finally found that by careful degassing of the tetrazene **10** (which does not incorporate oxygen rapidly, as does **11**), and using thermal decomposition at 65° for 72 hr (which corresponds to 4 half-lives for decomposition of **4** (X = H), **10** should decompose slightly more rapidly), we could generate samples of **11** ⇌ **12** in which no nitroxide was detectable. Controls indicated that appreciable decomposition of amino radical was not detected in 72 hr at 65°, although heating at higher temperatures did lead to irreversible disappearance of **12**.

The problems associated with quantitative esr are many, and have been discussed by the groups of Ingold[12] and Fessenden.[13] Data on rates may seldom be trusted to more than 10–20% accuracy, although higher precision is frequently possible. We used di-*tert*-butyl nitroxide in identical tubes in methylcyclohexane (the same solvent used for **11** ⇌ **12**) for concentration standards, and our methods for obtaining the K and k_2 are dealt with in the Experimental Section. We measured K over a 58° range, as summarized in Table II, and a plot of ln K *vs.* $1/T$ appears as Figure 2. The data yield least-squares values of $\Delta H° = 31.2$ kcal/mol, $\Delta S° = 73$ eu.

Table II. Equilibrium Data for **11** ⇌ **12**

Temp, °C	K, mol/l.	Temp, °C	K, mol/l.
103.2	1.09×10^{-2}	68.6	1.25×10^{-4}
91.8	2.79×10^{-3}	57.0	2.50×10^{-5}
80.5	6.39×10^{-4}	44.7	6.00×10^{-6}
68.6	1.58×10^{-4}		

Radical **12** could also be generated at lower temperatures by photolysis. We measured the rate of decay of the amino radical **12** over a 53° temperature range by monitoring disappearance of the esr signal after shutting off the lamp and found excellent linearity for second-order plots of the data (see Figure 3 for an example). The rate constants observed are summarized in Table III. A plot of these data as ln k_2/T *vs.* $1/T$ appears as Figure 4. Scatter is much more apparent in the rate constant plot of Figure 4. The equilibrium constant plots involve only a single concentration measurement, while the rate constants involve a large number of such measurements, so the loss in *precision* is not surprising, but the great scale expansion of the vertical axis in the rate constant plots should also be realized; k_2 is far less sensitive to temperature than is K. The least-squares line for the data of Figure 4 gives $\Delta H^{\ddagger} = -2.2$ kcal/mol, $\Delta S^{\ddagger} = -65$ eu.

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[11] (a) H. Wieland and M. Offenbacher, *Chem. Ber.*, **47**, 2111 (1914); (b) H. Wieland and A. Roseev, *ibid.*, **48**, 1117 (1915); (c) H. Wieland and K. Roth, *ibid.*, **53**, 210 (1920).

[12] (a) K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, **93**, 902 (1971); (b) D. F. Bowman, J. L. Brokenshire, T. Gillan, and K. U. Ingold, *ibid.*, **93**, 6551 (1971); (c) D. F. Bowman, T. Gillan, and K. U. Ingold, *ibid.*, **93**, 6555 (1971).

[13] R. W. Fessenden and R. H. Thomson, *J. Phys. Chem.*, **68**, 1508 (1964).

Table III. Second-Order Rate Constants for Decay of **12**

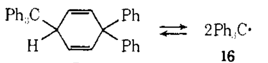
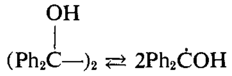
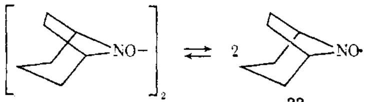
Temp, °C	k_2, l./(mol sec)
−13.8	1.18, 1.26, 1.41, 1.96
−21.0	1.28, 1.75, 1.78, 2.90
−29.0	1.76, 2.49, 1.83
−32.0	2.06, 2.21
−37.4	2.33, 2.80, 1.92, 2.70, 1.97, 2.37, 2.62, 62.1, 1.99, 1.78
−49.3	2.97, 2.41, 2.48, 2.49, 2.83
−50.0	2.07, 2.16, 1.84
−62.0	3.54
−66.8	4.11

Discussion

Tetrazene Decomposition. Our expectation that the substituent effect on **1** decomposition would be mostly removed in **4** because of a conformational effect has been fulfilled, both for *p*-methoxy and for *p*-cyano substituents. We do not feel that the small difference in rate observed for substituted **4** decompositions can be unambiguously interpreted.[5] It is worth pointing out that X-ray studies on **4** (2,4,6-trideuteriophenyl) and **4** (X = 4-Cl) have shown that at least in the solid, the conformation is close to that shown in **3**, with the N_1–N_2 bond nearly perpendicular to the plane of the aromatic ring.[14a] The substituent effect on *a*(N) has been amply discussed earlier.[1]

Amino Radical–Hydrazine Equilibrium. Relatively few examples of temperature effects upon radical disappearance rates have appeared in the literature, and in even fewer cases have the "termination" reactions, leading to disappearance of radicals, been observed to be second-order reactions. This area of research has been recently reviewed by Ingold.[14b] The thermodynamic parameters for the equilibria and dimerization reactions which seem most comparable with the case we have studied are summarized in Table IV.

Table IV. Thermodynamic Parameters for Some Radical–Radical Reactions

	$\Delta H°$	$\Delta S°$	Ref
 **15** **16**	+10.8	+24.5	*a*
 $(Ph_2C(OH)—)_2 \rightleftarrows 2Ph_2\dot{C}OH$ **17** **18**	+32.5 ± 1.7	23.9	*b*
$((CH_3CD_2)_2NO)_2 \rightleftarrows 2(CH_3CD_2)_2NO\cdot$ **19** **20**	+7.6	+24.8	12c
 **21** **22**	8.2 ± 0.3	25 ± 2	*c*
11 ⇄ 2 **12**	31.2 ± 2	73.6 ± 10	This work
Combination reactions	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	Ref
2 **16** ⇄ **15**	6.1	−26	*a*
2 **18** ⇄ **17**	1.0 ± 0.5	−6.4	*b*
2 **12** ⇄ **11**	−2.2 ± 1	−65.4 ± 10	This work

[a] F. S. D'iachkovskii, N. N. Bubnov, and A. E. Shilov, *Dokl. Akad. Nauk SSSR*, **122**, 629 (1958). [b] S. A. Weiner, *J. Amer. Chem. Soc.*, **93**, 6978 (1971). [c] G. D. Mendenhall and K. U. Ingold, *J. Amer. Chem. Soc.*, **94**, 7166 (1972).

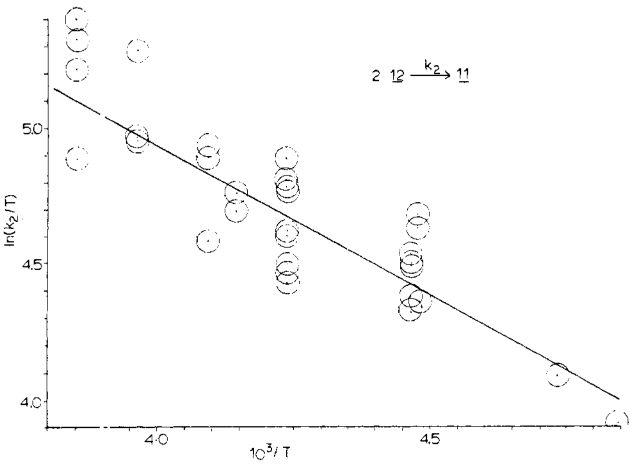


Figure 4. Plot of $-\ln(k_2/T)$ *vs.* $10^3/T$ for the second-order rate constants of Table III.

The observed $\Delta H°$ value of **11** ⇄ **12** of 31 kcal/mol seems entirely consistent with expectation; the bond strength for the N–N bond of hydrazobenzene has been calculated to be 37.7 kcal/mol from heats of combustion,[15] and *tert*-butyl substitution ought to lower this value somewhat. The $\Delta S°$ value observed is astonishingly high. Hydrazine **11** is far more hindered than the other cases shown, and cleavage should free rotation of the *tert*-butyl groups substantially. The dimerization activation parameters are also highly unusual. Negative activation energies have been observed in other radical–radical reactions, such as those of nitroxides[12c] and phenoxy radicals,[16] and have been interpreted quite reasonably in terms of equilibria preceding the slower step of the reaction. Although there is a lot of scatter in our data, we believe that we have established that **12**

(14) (a) Determined by R. T. Landis and J. Calabrese, to be reported separately. (b) K. U. Ingold in "Free Radicals," J. K. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1972, Chapter 2.

(15) L. G. Cole and E. C. Gilbert, *J. Amer. Chem. Soc.*, **73**, 5423 (1951).

(16) G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *ibid.*, **86**, 964 (1964).

dimerizes slightly more rapidly as the temperature is lowered, and that the observed $\Delta H^{\ddagger}$ is thus negative. A perfectly plausible way of explaining this would be that C–C or N–C bond formation with the aryl ring carbons is indeed the kinetically preferred mode of reaction, and that rearrangement to the stabler product takes place from this dimer, which does not build up to a high concentration. This explanation would be similar to that actually supported by the experiments of Mahoney and Weiner[17] for aryloxy radical terminations (which are first order). We wish to point out, however, that it would also seem possible that instead of having a σ-bonded dimeric intermediate accounting for the negative $\Delta H^{\ddagger}$ in our case, that **12** is probably not in the proper steric configuration for rapid dimer formation, and that a conformational change might be required in one or both amino radicals prior to combination to the hydrazine. The −65-eu $\Delta S^{\ddagger}$ observed for this reaction certainly indicates that a very restricted transition state is somehow involved. The prior conformational change argument is more or less the converse of the argument proposed[3] for **1** decomposition, in which we feel it has been established that a conformational change occurs before radical cleavage, and this effect dominates the kinetics observed for the reaction. Virtually no enthalpy of activation is involved in the reaction 2 **12** → **11**; the rate is almost entirely controlled by the large entropy of activation. The huge positive $\Delta S°$ of the **11** ⇄ **12** equilibrium and the correspondingly huge negative $\Delta S^{\ddagger}$ for the dimerization balance each other, and lead to quite ordinary appearing calculated values of $\Delta H^{\ddagger} = 29$ kcal/mol, $\Delta S^{\ddagger} = +8$ eu for the cleavage of the dimer, **11** → 2 **12**. This cancellation of the unusual aspects of the thermodynamic parameters observed for the equilibrium and dimerization gives us confidence that the numbers observed are at least qualitatively correct.

Experimental Section

Melting points employed a Thomas-Hoover Unimelt capillary apparatus. A Beckman IR-8 was used for ir spectra, Varian A60A, XL100, and Jeolco MH.100 equipment for nmr spectra, an AEI MS 902 for mass spectra, and Varian E.3 or E.15 for esr spectra. The lamp used for photolytic generation of **11** was a Hanovia 2500-W mercury-xenon compact arc lamp provided with a 15-cm water filter. Temperatures were maintained for kinetic studies using the standard Varian cold nitrogen flow system but temperatures were measured with a thermocouple and potentiometer. Rate constants and simulated esr spectra were calculated using the Madison Academic Computer Center's Univac 1108 computer.

***N*-*tert*-Butyl-3-methoxyaniline** was prepared by successive treatments of the aniline with *tert*-butyl iodide, using the reaction conditions employed for the *p*-bromo compound.[1] After treatment with four batches of *tert*-butyl iodide, the product was isolated by distillation: bp 97° (0.45 mm); nmr δ 1.33 (9 H, s), 3.28 (1, H, br s), 3.69 (3 H, s), 6.30–6.12 (3 H, complex), 6.91 (1 H, mult); ir (CCl_4) 2.86 and 2.93 μ.

***N*-Nitroso-*N*-*tert*-butyl-3-methoxyaniline** was prepared by N-nitrosation using the conditions for the *p*-bromo case[1] in 72% yield: mp 62.3–62.6°; nmr δ 1.56 (9 H, s), 3.74 (3 H, s), 7.30–7.10 (4 H, complex); ir 3.34 and 3.52 μ.

***N*-Amino-*N*-*tert*-butyl-3-methoxyaniline.** Room temperature reduction of the nitroso compound in ether led to a 6:1 mixture of hydrazine–amine, as indicated by nmr. Partial nmr: δ 1.13 (9 H, s), 3.75 (3 H, s).

1,4-Di-*tert*-butyl-1,4-bis-3-methoxyphenyl-2-tetrazene (4, X = 3-OMe) was prepared in 45% yield from the above mixture of hydrazine and amine by quinone oxidation:[1] mp (ethanol) 106.5–107.5° dec; nmr (δ, CCl_4) 1.04 (18.H, s), 3.78 (6 H, s), 6.80–6.50 (6 H, complex), 5.20 (2 H, ca-t, *J* = 9 Hz); uv (EtOH) 303 nm (ε 5000), 277 (6000), 237 (8700); ir 3.35 μ. *Anal.* Calcd for $C_{22}H_{32}N_4O_2$: C, 68.7; H, 8.39; N, 14.6. Found: C, 66.7; H, 8.22; N, 14.1.

***N*-*tert*-Butyl-*N*-nitroso-3-chloroaniline** was prepared by nitrosation[1] of the *tert*-butylaniline (bp 80° (0.04 mm)) in 70% yield: mp 72.5–73.2°; nmr δ 1.60 (9 H, s), 6.72 (2 H, complex), 7.35 (2 H, complex); ir 3.28 and 3.36 μ.

1,4-Di-*tert*-butyl-1,4-bis(3-chlorophenyl)-2-tetrazene (4, X = 3-Cl) by oxidation of the $LiAlH_4$ reduction mixture of the *N*-nitroso compound (which contained 75% NNH_2, 18% NH, and 3% NNO compound by nmr analysis) with quinone:[1] mp (ethanol) 109–110.5° dec; nmr (CCl_4) δ 1.08 (18 H, 5),7.35–6.76 (8 H, complex); ir 3.35 μ; uv (EtOH) λ_{max} 311 nm (ε 5600), 250 (8500). *Anal.* Calcd for $C_{20}H_{24}N_4Cl_2$: C, 61.07; H, 6.66; N, 14.24; Cl, 18.03. Found: C, 61.05; H, 6.55; N, 14.22; Cl, 18.09.

3,5-Di-*tert*-butylbromobenzene (8) was prepared from 3,5-di-*tert*-butylphenol (**7**) by the method of Wiley and coworkers.[16] To 50.6 g (0.194 mol) of triphenylphosphine, slurried in 170 ml of acetonitrile in a 500-ml three-necked, round-bottomed flask with mechanical stirrer, condenser, and nitrogen inlet, cooled to 0°, 31 g (0.191 mol) of bromine was added dropwise. After the mixture was stirred for 1 hr, 40 g (0.194 mol) of **7** in 125 ml of acetonitrile was added over 30 min, and the acetonitrile was distilled off, at a bath temperature of 130°. The flask was heated in a Wood's metal bath at 340° for 18 hr, the escaping HBr being bubbled into water. After cooling to 100°, the reaction mixture was poured into an 8-in. crystallizing dish, the solid was broken up and triturated with 1 l. of pentane, and the pentane was dried with magnesium sulfate and passed through a 25 mm × 35 cm column of alumina. The pentane was evaporated and the residue distilled, giving 30 g (59%) of colorless **8** (bp 91° (0.95 mm)), which solidified, mp 62.8–64°; nmr δ 1.32 (18 H, s) and 7.26 (3 H, s).

***N*,3,5-Tri-*tert*-butylaniline (9)** was prepared by the general method of Biehle and coworkers.[18] To a stirred mixture of 3.9 g (0.1 mol) of sodium amide and 100 ml of *tert*-butylamine was added 13.45 g (0.05 mol) of **8**, and the mixture was heated at reflux under nitrogen for 10 hr, cooled, and quenched with 7.5 g of ammonium chloride. After distillation of excess solvent, 200 ml of ether was added, and the mixture was stirred for 10 min and filtered. The filtrate was dried with magnesium sulfate and distilled, giving 8.6 g (66%) of **9**: bp 111° (2 mm); nmr δ 1.28 (18 H, s), 1.30 (9 H, s), 3.22 (1 H, br s), 6.44 (2 H, d, *J* = 1 Hz), 6.70 (1 H, t, *J* = 1 Hz); ir 2.91 μ.

1,4-Bis(3,5-di-*tert*-butylphenyl)-1,4-di-*tert*-butyl-2-tetrazene was prepared in an entirely analogous fashion to **4** (4-Br).[1] *N*-Nitroso-**9**, mp 114.5–115.5°, was prepared in 59% yield, was reduced to a 24% yield of *N*-amino-**9**, and oxidized without purification to give a 56% yield of **10**: mp 154–155°; nmr (CCl_4) δ 1.02 (18 H, s), 1.32 (36 H, s), 6.79 (24 H, d, *J* = 2 Hz), 7.11 (1 H, t, *J* = 2 Hz); ir 3.35 μ; uv (ethanol) λ_{max} 248 nm (ε 20,000), 310 (1000). *Anal.* Calcd for $C_{36}H_{60}N_4$: C, 78.78; H, 11.02; N, 10.21. Found: C, 78.18; H, 10.98; N, 10.14.

1,2-Di-*tert*-butyl-1,2-bis(3,5-di-*tert*-butylphenyl)hydrazine (11) was prepared as follows. A sample of *N*-chloro-*N*,3,5-di-*tert*-butylaniline was prepared by stirring the amine **9** with a 20-fold excess of calcium hypochlorite for 24 hr at −15°, filtering, and removing the solvent (nmr δ 1.20 (9 H, s), 1.48 (18 H, s), 7.08 (3 H, br s)). A solution of this substance in 15 ml of dry THF was added to a solution of 1.0 g of amine **9** in 50 ml of THF which had been treated with 3.05 ml of commercial *n*-butyllithium solution (3.8 mmol), and cooled to −78°. The solution turned red-brown; after 4 hr, an excess of ammonium chloride was added, and the mixture was filtered and evaporated to a residue; the mixture was separated by tlc on silica gel (benzene). The most rapidly moving band was separated and gave 560 mg of **11**: mp 142°; nmr (CCl_4) δ 1.25 (18 H, s), 1.50 (9 H, s), 6.66 (1 H, m), 6.78 (2 H, m); ir (CCl_4) 3.37 μ; mass spectrum *m/e* (% of largest peak) 520 (9), 246 (75), 57 (100). This material was quite sensitive to air, and later esr experiments indicated that some incorporation of oxygen and formation of mixed nitroxide–amino radical dimer had occurred.

Generation of Authentic *N*,3,5-Tri-*tert*-butyl Nitroxide (13) Esr Spectrum. For comparison with the spectra generated by admission of air to decomposing mixtures of **11** and **10**, we prepared a pentane solution of **13** as follows: 500 mg of aniline **9** in 20 ml of chloroform was treated with 1.31 g of 50% pure *m*-chloroperbenzoic acid. The resulting red-brown solution was stirred for 16 hr and

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(17) L. R. Mahoney and S. A. Weiner, *J. Amer. Chem. Soc.*, **94**, 585 (1972).

(18) E. R. Biehle, P. Patrizi, and P. C. Reeves, *J. Org. Chem.*, **26**, 3252 (1971).

evaporated, and the pentane extracts of the residue had an esr spectrum indistinguishable from that formed upon heating **10** in poorly degassed sample tubes.

11 → 12 Kinetics. Samples of **10** were weighed into esr tubes, fixed to the vacuum line (diffusion pump), and filled to a precalibrated mark by bulb-to-bulb distillation of methylcyclohexane from a sample previously freeze–pump–thaw cycle degassed. After 4–6 further freeze–pump–thaw cycles, the tubes were sealed under vacuum. A series of seven di-*tert*-butyl nitroxide samples (vpc pure) were prepared by successive dilutions in volumetric glassware, degassed before sealing, and stored at $-10°$. The appropriate instrument settings for best display of the initial radical concentration were determined; a sample of standard was placed in the spectrometer and the low-field line was run twice and the peak-to-peak height measured. The low-field peak of the sample of **11** was then run with the same instrument settings; the concentration of **11** was determined by use of peak-to-peak height and the proper intensity factors (1:3 for the nitroxide standard, 1:24 for **11**). Separate control calibrations demonstrated that $<5\%$ error was introduced by measuring only the low-field peaks, and that peak-to-peak heights were linear with area under integrated (absorption) peaks for **11**. Comparison of concentration obtained by use of peak-to-peak heights and areas under integrated (absorption) curves showed that use of peak-to-peak heights introduced $<10\%$ difference, with no systematic deviations detected as a function of temperature. Corrections to the standard concentration because of volume changes with temperature were obtained from the literature.[19] All concentration measurements had both sample and standard at the same temperature. A single cavity esr probe was employed, alternating standard and sample tubes. No provision was made for the effects of minor variations of field strength, but this is not felt to significantly affect our concentration measurements.

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work, as well as the Major Instrument Program of the National Science Foundation for funds used in purchasing spectrometers employed.

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Reaction of Hydrogen Peroxide with Alkyl Sulfonate Esters[1,2]

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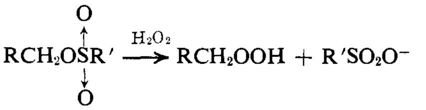
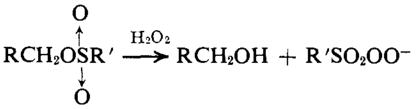
Abstract: The chemistry between a typical sulfonate ester, *n*-butyl methanesulfonate, and hydrogen peroxide in neutral and basic aqueous solutions was examined. Hydrogen peroxide itself at 0.64 *M* has no effect on the ester; *n*-butyl alcohol, the sole product below pH 10, is formed at the same rate as in the absence of peroxide. Above pH 11 *n*-butyl hydroperoxide is formed quite rapidly as the sole product, arising from attack by HO_2^-. The second-order rate constant for HO_2^- attack at 25° in water is $96 \pm 13 \times 10^{-5}\ M^{-1}\ sec^{-1}$, some 55 times greater than the HO^- rate constant. This, combined with the much lower pK_a (11.57) of H_2O_2 than water, produces hydroperoxide quantitatively. The reaction proceeds solely by alkyl–oxygen, and not sulfur–oxygen, scission. An attempt to observe S–O scission was made by examining neopentyl methanesulfonate in 40% *tert*-butyl alcohol at a nominal pH of 12.5 with about 0.3 $M\,H_2O_2$. Neither loss of ester nor formation of product was observed in 21 days.

A previous publication[3] and the accompanying paper describe the reaction of hydrogen peroxide with serine-195 sulfonated chymotrypsin. Because of the possibility of attack at sulfur by peroxide in that reaction, we undertook an examination of the chemistry of primary organic sulfonates with hydrogen peroxide especially under conditions analogous to these used in the protein study. From previously known chemistry and established synthetic routes,[4,5] it was anticipated that the major path would be S_N2 attack at carbon to produce alkyl hydroperoxide (eq 1), but another possibility was attack at sulfur (eq 2) to produce alcohol and persulfonate (which would rapidly decompose). That the alkyl hydroperoxide should be reasonably stable under the reaction conditions was predicted from earlier studies and confirmed.



$$RCH_2O\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}R' \xrightarrow{H_2O_2} RCH_2OOH + R'SO_2O^- \qquad (1)$$



$$RCH_2O\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}R' \xrightarrow{H_2O_2} RCH_2OH + R'SO_2OO^- \qquad (2)$$

Another aspect of the work was to investigate the reality and magnitude of the enhanced nucleophilicity of hydroperoxide ion in S_N2 attack at the saturated carbon, since at the outset of our work there had been only one report concerning this phenomenon.[6]

Experimental Section

Materials. *n*-Butyl alcohol and 30% hydrogen peroxide were Mallinckrodt reagents. *n*-Butyl hydroperoxide, *n*-butyl methanesulfonate, and neopentyl methanesulfonate were prepared by the procedure of Williams and Mosher.[7] Buffer solutions were made with double distilled water and analytical grade reagents. All

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(1) (a) This research was supported by the Research Corporation and the Intramural Fund of the University of California. (b) Abstracted in part from the Ph.D. Thesis of N. A. R., March 1973.

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