ethylamines were obtained approximately in the ratio 1:4:6. In the latter case di- and triethylamines were obtained in approximately a 1:1.6 ratio. Total yield from the ammonia or ethylamine derivatives of IIb and IIc ranged from 25 to 10%.

In the case of the derivative obtained by addition of triethylamine to the complex IIa the crude tetraethylammonium hydrochloride obtained by method 2 was dissolved in a small amount of ethanol. To this solution a cold saturated solution of picric acid in ethanol was added. After removal of the solvent *in vacuo*, the dried residue was recrystallized from ethanol–ether. The identification was carried out by comparing the powder pattern of this material with that of an authentic sample.

Acknowledgment. This work was performed with the financial support of Italian CNR. Thanks are given to Mr. Nunzio Lanzetta for his experimental assistance.

Calorimetric Study of the 2,4,6-Tri-*t*-butylphenoxy Radical in Solution

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Contribution from the Scientific Laboratory, Ford Motor Company, Dearborn, Michigan 48121. *Received October 25, 1969*

Abstract: Direct experimental determinations of the differences in the heats of formation in solution of a free radical and its hydrogenated precursor have been carried out for the first time. The method consists of calorimetric measurements of the heat of the quantitative reaction of hydrazobenzene with 2,4,6-tri-*t*-butylphenoxy radical (I) to produce *trans*-azobenzene and 2,4,6-tri-*t*-butylphenol (II). Values of $(\Delta H_f)_{II^s} - (\Delta H_f)_{I^s}$ calculated from these studies vary from 28.13 ± 0.13 kcal/mol in pure carbon tetrachloride to 29.73 ± 0.07 kcal/mol in the mixed solvent carbon tetrachloride–dioxane (mole fraction 0.53). Calorimetric studies of the reaction of 4-*t*-butylphenol with I to produce II and 4-(4-*t*-butylphenoxy)-2,4,6-tri-*t*-butyl-2,5-cyclohexadiene-1-one (IV) were also carried out in a number of solvents and the results of those studies are internally consistent with the results of the hydrazobenzene reaction. A comparison of the solution properties of I with those of 1,3,5-tri-*t*-butylbenzene (V) reveals that specific solvent interactions with the radical due to its free electron are small (±0.5 kcal/mol) and thus V is a good model for I in solution. The difference in the heats of formation of a number of other stable free radicals, B·, and the molecules from which they are formed, BH, is then calculated by combining the results of the present study and the results of earlier studies of the reactions of I with BH to produce II and B·. The strain energy in II associated with steric interaction of 2,6-di-*t*-butylphenol group is calculated in the gas phase as equal to 8.0 ± 2.0 kcal/mol. The manifestations of this strain energy in the phenomena of the synergistic behavior of mixtures of hindered and nonhindered phenols as antioxidants and the ease of disassociation of dimers derived from 2,5-di-*t*-butylphenoxy radicals are then discussed.

The values of the bond energies of organic molecules and the heats of formation of the free radicals and atoms derived from them are of considerable theoretical and practical interest. Determinations of such quantities have been limited exclusively to the gas phase since the conventional techniques are based upon either the pyrolysis of the parent molecule or the thermal formation of atoms from a diatomic molecule such as I_2.[1] Among the limitations of these gas-phase techniques are (1) they are confined to systems where the reactants and products are of moderately low molecular weight, and (2) the parent molecule must not contain bonds which are less thermally stable at elevated temperatures than the bond whose energy is to be determined. For these reasons the development of techniques for the determination of the heats of formation of free radicals at moderately low temperatures, *i.e.*, in the liquid phase where such limitations may be circumvented, would be very desirable.

In contrast to most free radicals, solutions of the 2,4,-6-tri-*t*-butylphenoxy radical (I) may be prepared and these solutions are stable in the absence of oxygen and other reactive compounds. As a result of this unique property a classical approach to the heat of formation of I may be taken, *i.e.*, the heat of its reaction can be directly measured in systems for which the heats of formation of the other reactants and products are known or may be determined. Since I engages in reversible hydrogen atom transfer reactions with many reactive organic compounds, *i.e.*, hydroperoxides[2] and phenols,[3] to form 2,4,6-tri-*t*-butylphenol (II) and the corresponding oxy radical, the heats of formation of a variety of free radicals not amenable to study by the usual gas-phase techniques may be determined if the difference in the heats of formation of I and II is known.

The present work describes the direct calorimetric determination of the differences in the heats of formation of I and II in a variety of solvents. A combination of the results of this study with the results of earlier equilibrium studies of I and II with other stable free radicals has led to values of the difference in the heats of formation in solution of a number of these free radicals and their hydrogenated precursors. In addition a quantitative estimate of the strain energy present in II has been obtained and its significance in the chemical reactions of II has been analyzed.

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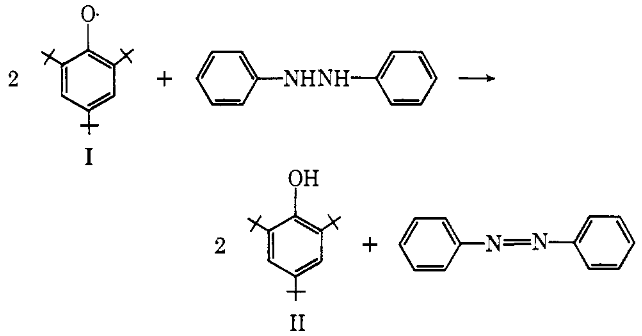
[1] D. M. Golden, R. Walsh, and S. W. Benson, *J. Am. Chem. Soc.*, 87, 4053 (1965).

[2] L. R. Mahoney and M. A. DaRooge, *ibid.*, 89, 5619 (1967).

[3] M. A. DaRooge and L. R. Mahoney, *J. Org. Chem.*, 32, 1 (1967).

Results and Discussion

Reactions Utilized for Calorimetric Study. In the present work two reactions have been utilized for the calorimetric study of the 2,4,6-tri-*t*-butylphenoxy radical. The first reaction is the very rapid reaction of hydrazobenzene with 2,4,6-tri-*t*-butylphenoxy (I) which has been reported[4,5] to form 2,4,6-tri-*t*-butylphenol (II) and azobenzene.



I

II

The heats of formation are 52.9, 86.59, and 76.49 kcal/mol at 298°K for hydrazobenzene and *cis*- and *trans*- azobenzenes,[6] respectively. Thus a determination of the heat of the reaction will yield the difference in the heat of formation of II and I provided the reaction is quantitative and the relative amounts of *cis*- and *trans*-azobenzenes produced in the reaction are known.

Müller and Ley[4] reported that the titration of a benzene solution of the radical, prepared from a solid sample of the radical, with a solution of hydrazobenzene under nitrogen yielded an end point which corresponded to approximately 95% of theory. However, as they point out, the end point of the titration was not sharp and the preparation of pure radical in the solid state is very difficult. Cook and Norcross[5] utilized the reactions of hydrazobenzene with solutions of 2,4,6-tri-*t*-butylphenoxy to obtain the extinction coefficient of the phenoxy radical. These workers reported an increase in absorbance with time in their spectrophotometric analysis for azobenzene and they suggested that the *trans*-azobenzene produced in the reaction was photoisomerized in the spectrophotometer to produce *cis*-azobenzene which has a much higher extinction coefficient than the *trans* isomer. Although photolysis of their solutions to a photostationary state and comparison with standard solutions demonstrated that the reaction to form azobenzene was quantitative, it is not clear whether the product initially produced is exclusively in the *trans* form.

We have been able to demonstrate that a quantitative yield of *trans*-azobenzene is formed from hydrazobenzene under the conditions of our calorimetric experiments. A solid sample of hydrazobenzene was dissolved in solution containing an excess of the 2,4,6-tri-*t*-butylphenoxy radical. The excess radical is then destroyed by reaction with 2,6-di-*t*-butylphenol. These operations were carried out with the exclusion of light and in an argon atmosphere. The spectrum of the resulting solution was recorded between 5000 and 4000 Å, utilizing as a reference solvent a sample of the same radical solution which was carried through the same procedure, excluding the hydrazobenzene. The spectra obtained were superimposable with those obtained from pure *trans*-azobenzene. The absorbance of the sample did not change with exposure to the light of the spectrophotometer and it was possible from the absorption maxima at 4500 Å to determine the yield of *trans*-azobenzene based on hydrazobenzene. As shown in Table I, a quantitative yield of the *trans* isomer is obtained in the solvents reported in the present study.

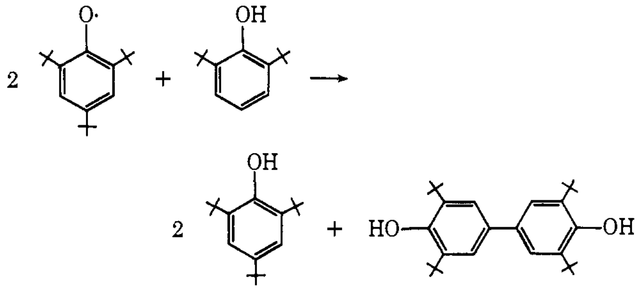
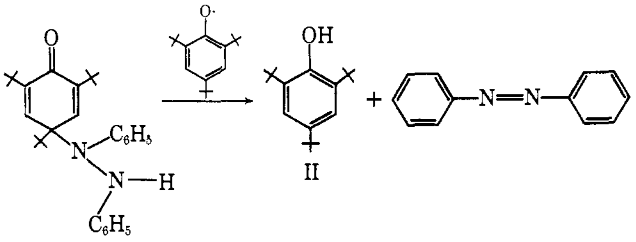


Table I. Yield of *trans*-Azobenzene Formed in the Reaction of 2,4,6-Tri-*t*-butylphenoxy Radical with Hydrazobenzene

Solvent	Mole of hydrazobenzene × 10^3	Mole of *trans*-azobenzene × 10^3	%
CCl_4	0.279	0.277	99.4
	0.295	0.293	99.2
	0.529	0.525	99.2
	0.540	0.540	100.0
C_6H_5Cl	0.280	0.281	100.4
	0.280	0.283	101.1
	0.283	0.286	100.9
	0.337	0.339	100.5
C_6H_6	0.237	0.239	101.0
	0.249	0.245	98.4
	0.345	0.348	100.8
CCl_4-$C_4H_8O_2$[a]	0.212	0.216	101.8
	0.249	0.244	97.8
	0.335	0.341	101.8
CCl_4-CH_3CN[b]	0.299	0.301	100.8
	0.323	0.326	101.0
	0.352	0.354	100.5

[a] Mole fraction of dioxane equal to 0.5317. [b] Mole fraction of acetonitrile equal to 0.6486.

Our results and those of Cook and Norcross are readily accounted for by the following considerations. In analogy with the formation of quinol ethers in the reaction of I with phenols,[3] at least a fraction of the reaction of I with the radical derived from hydrazobenzene should proceed through the intermediate III. Under conditions of our experiments, *i.e.*, excess of I, the intermediate would react with the excess I to form directly *trans*-azobenzene, *i.e.*



III

II

In contrast, under the conditions of the experiments of Cook and Norcross, *i.e.*, excess hydrazobenzene, the

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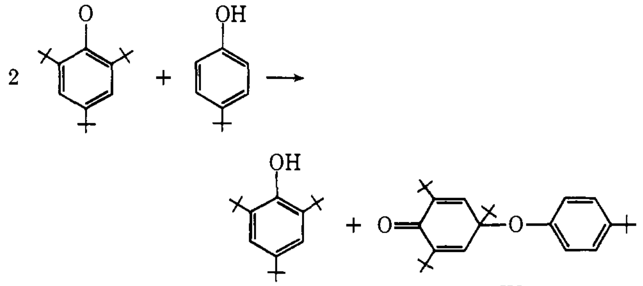
[4] E. Müller and K. Ley, *Chem. Ber.*, **87**, 922 (1954).

[5] C. D. Cook and B. E. Norcross, *J. Am. Chem. Soc.*, 81, 1176 (1959).

[6] L. G. Cole and E. C. Gilbert, *ibid.*, 73, 5423 (1951).

intermediate III would thermally and/or photochemically decompose to form II and azobenzene in a slow step.

The second reaction studied in the present work is that of 4-*t*-butylphenol with the 2,4,6-tri-*t*-butylphenoxy radical. Earlier work from our laboratory demonstrated that a yield greater than 95% of 4-(4-*t*-butylphenoxy)-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one (IV) was produced in the reaction.[3] Moreover, since tlc and glpc failed to reveal even trace amounts of phenolic dimers derived from 4-*t*-butylphenol the reaction is likely to be quantitative as written. The heat of formation of IV has not been determined; thus the reaction cannot be utilized for a determination of the heat of formation of I. We have chosen this reaction primarily to test the internal consistency of the results of calorimetric determinations from the hydrazobenzene reaction in different solvents.



IV

Thermochemical Relationships. For calorimetric studies of reactions which are carried out in solution it is necessary to define the solvent and to specify the state of dilution of the reactants and of the products in the solvent. All the quantities reported in the present work refer to the state of infinite dilution. The partial molal enthalpy of solution at infinite dilution of compound i is defined by the expression

$$(\Delta\bar{H}_{\text{solution}})_i^s = \lim_{n_i \to 0}\left(\frac{Q}{n_i}\right)_{T,m}$$

where Q is equal to the heat absorbed or evolved upon dissolving n moles of compound i in a solution containing m moles of solvent s at temperature T. The heat of formation of a compound in the state of infinite dilution in a solvent is equal to its enthalpy of formation in its standard state at 280 °K plus its experimentally determined partial molal enthalpy of solution at infinite dilution in solvent s, *i.e.*

$$(\Delta H_f)_i^s = \Delta H_f^0 + (\Delta\bar{H}_{\text{solution}})_i^s \qquad (1)$$

Let the superscript CCl_4 denote the enthalpy changes in carbon tetrachloride and the superscript s represent the enthalpy changes in a second solvent, *i.e.*, benzene, chlorobenzene, etc. Then from eq 1

$$(\Delta H_f)_i^s - (\Delta H_f)_i^{CCl_4} = (\Delta\bar{H}_{\text{solution}})_i^s - (\Delta\bar{H}_{\text{solution}})_i^{CCl_4} \qquad (2)$$

Three quantities may be obtained from the results of the present study. They are (1) the effect of solvent upon the enthalpy of formation of the 2,4,6-tri-*t*-butylphenoxy radical, $(\Delta H_f)_I^s - (\Delta H_f)_I^{CCl_4}$, (2) the difference in the heat of formation of the 2,4,6-tri-*t*-butylphenoxy radical and 2,4,6-tri-*t*-butylphenol as a function of solvent, $(\Delta H_f)_I^s - (\Delta H_f)_{II}^s$, and (3) the absolute value of the heat of formation in solution of the 2,4,6-tri-*t*-butylphenoxy radical, $(\Delta H_f)_I^s$.

In the present work a solid sample of BH, *i.e.*, hydrazobenzene or 4-*t*-butylphenol, is dissolved in a solution of excess I and the reaction occurs

$$2\text{I} + \text{BH(solid)} \longrightarrow \text{products} + \Delta H_{\text{reaction}}$$

and

$$(\Delta H_{\text{reaction}})^s = \Sigma(\Delta H_f)^s_{\text{products}} - 2(\Delta H_f)_I^s - (\Delta H_f)_{BH}^s \qquad (3)$$

Under these conditions the heat generated *per mole of BH*, $(\Delta\bar{H}_{\text{obsd}})^s$, is related to the $(\Delta H_{\text{reaction}})^s$ by the equation

$$(\Delta H_{\text{reaction}})^s = (\Delta\bar{H}_{\text{obsd}})^s - (\Delta\bar{H}_{\text{solution}})_{BH}^s \qquad (4)$$

Combining eq 3 and 4, substitution of $\Sigma(\Delta H_f)_{\text{product}}$ and $(\Delta H_f)_{BH}^s$ by $(\Delta H_f)_i^\circ$ and $(\Delta H_{\text{solution}})_i$, eq 1, and rearranging yield the general expression for the value of $(\Delta H_f)_I^s$

$$(\Delta H_f)_I^s = 0.5\{-(\Delta H_{\text{obsd}})^s + \Sigma(\Delta H_{\text{solution}})^s_{\text{products}} - (\Delta H_f)_{BH}^\circ + \Sigma(\Delta H_f)^\circ_{\text{products}}\}$$

Therefore

$$(\Delta H_f)_I^s - (\Delta H_f)_I^{CCl_4} = 0.5\{(\Delta H_{\text{obsd}})^{CCl_4} - (\Delta H_{\text{obsd}})^s - \Sigma(\Delta\bar{H}_{\text{solution}})_{\text{products}}^{CCl_4} + \Sigma(\Delta H_{\text{solution}})^s_{\text{products}}\} \qquad (5)$$

Note that the value of this quantity does not depend upon the knowledge of the heats of formation of the products or BH, but only upon the heat evolved for the reaction in the two solvents and upon the experimentally determined heats of solution of the products in the two solvents.

The values of the second quantity, $(\Delta H_f)_I^s - (\Delta H_f)_{II}^s$, require a knowledge of the heats of formation of azobenzene (Az) and hydrazobenzene (H_2Az) in their standard states as solids at 298 °K

$$(\Delta H_f)_I^s - (\Delta H_f)_{II}^s = 0.5\{(\Delta H_f)_{Az}^\circ - (\Delta H_f)_{H_2Az}^\circ + (\Delta H_{\text{solution}})_{Az}^s - (\Delta H_{\text{obsd}})^s\} \qquad (6)$$

The third quantity, $(\Delta H_f)_I^s$, requires a determination of the heat of formation of 2,4,6-tri-*t*-butylphenol in its standard state as a solid at 298 °K. The value of that quantity is equal to −113.1 ± 0.9 kcal/mol.[7]

Partial Molal Enthalpies of Solution and Observed Heats of Reaction. In Table II are summarized the values of the partial molal enthalpies of solution at infinite dilution, $(\Delta\bar{H}_{\text{solution}})_i^s$, at 298 °K experimentally determined for the compounds utilized in the present study.

The introduction of solid hydrazobenzene or 4-*t*-butylphenol into a solution of excess 2,4,6-tri-*t*-butylphenoxy radical in the calorimeter under argon results in a rapid evolution of heat. Examination of the time–temperature curves failed to reveal any process in which heat is evolved or absorbed after the initial reaction.

Systematic variation of the quantity of hydrazobenzene and 4-*t*-butylphenol revealed that the quantities of heat evolved are proportional to the amounts of these materials dissolved in the calorimeter (*cf.* Figure 1). To assure that the observed heats are not a function of

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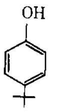
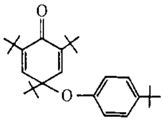
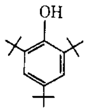
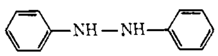
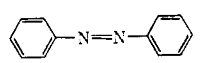
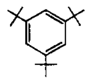
(7) The authors thank Dr. G. Sinke of Dow Chemical Company, Midland, Mich., for a determination of the heat of combustion of solid 2,4,6-tri-*t*-butylphenol.

Table II. Partial Molal Enthalpies of Solution at Infinite Dilution, $(\Delta \bar{H}_{\text{solution}})_i^s$, for the Solids Utilized in Calorimetric Study

	$(\Delta H_{\text{solution}})_i^s$, kcal/mol					
Compound	CCl_4	C_6H_6	C_6H_5Cl	C_6H_5Cl-tetralin[a]	$C_4H_8O_2$-CCl_4[b]	CH_3CN-CCl_4[c]
	6.82 ± 0.08	5.23 ± 0.06	5.72 ± 0.10			
	4.91 ± 0.08	5.40 ± 0.08	4.65 ± 0.04			
	2.61 ± 0.06 (2.57 ± 0.05)[d]	3.15 ± 0.12	2.21 ± 0.11	2.15 ± 0.04	1.82 ± 0.05	2.83 ± 0.09
	6.13 ± 0.10	4.71 ± 0.05	5.31 ± 0.04	5.38 ± 0.07		
	5.28 ± 0.02 (5.28 ± 0.02)[d]	5.04 ± 0.05	4.88 ± 0.07	5.24 ± 0.01	5.57 ± 0.05	5.88 ± 0.06
	1.68 ± 0.04	2.81 ± 0.08	2.06 ± 0.06	2.35 ± 0.02	3.06 ± 0.08	2.75 ± 0.02

[a] Mole fraction of tetralin equal to 0.3350. [b] Mole fraction of dioxane equal to 0.5317. [c] Mole fraction of acetonitrile equal to 0.6486. [d] In 0.24 *M* solution of I.

the concentration of 2,4,6-tri-*t*-butylphenoxy radical, a systematic study of the value of $(\Delta \bar{H}_{\text{obsd}})^s$ as a function of the concentration of 2,4,6-tri-*t*-butylphenoxy was carried out. As shown in Table III, an 18-fold variation in the radical concentration did not result in any significant variation in the value of $(\Delta \bar{H}_{\text{obsd}})^{CCl_4}$. We therefore conclude that the 2,4,6-tri-*t*-butylphenoxy radical is in the state approximating infinite dilution under the conditions of the calorimetric experiments.

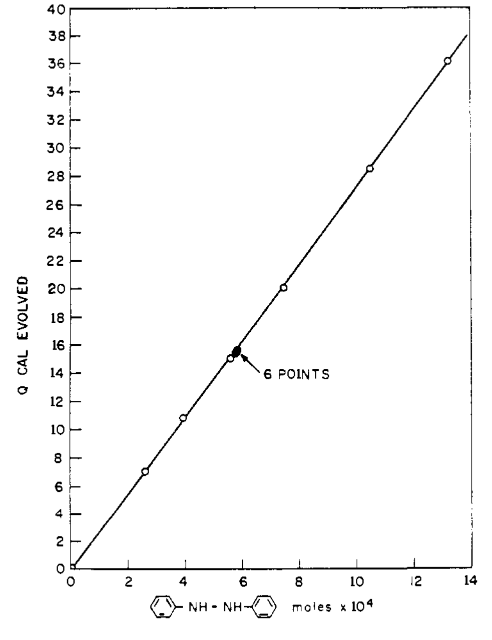


Figure 1. Heat evolved in the calorimeter in the reaction of hydrazobenzene (solid) with excess I in carbon tetrachloride.

Table III. Effect of the Concentration of 2,4,6-Tri-*t*-butylphenoxy on the Value of ΔH_{obsd} in CCl_4 at 298°K[a]

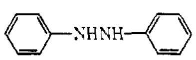
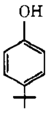
Moles of I × 10^4	Moles of hydrazobenzene × 10^4 added	Cal evolved	ΔH_{obsd}, kcal/mol
409.0	5.786	15.82	27.34
408.0	5.755	15.76	27.38
75.4	5.609	15.47	27.57
46.5	5.745	15.89	27.65
37.0	5.723	15.71	27.49
27.7	5.767	15.76	27.33

[a] The volume of solution in the calorimeter was equal to 200.0 ml in all cases.

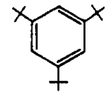
In Table IV are summarized the values of $(\Delta H_{\text{obsd}})^s$, the quantity of heat generated per mole of hydrazobenzene or 4-*t*-butylphenol dissolved in the calorimeter containing excess radical in various solvents at 298°K. Also listed are the values of $(\Delta H_f)_I^s - (\Delta H_f)_I^{CCl_4}$, $(\Delta H_f)_I^s - (\Delta H_f)_{II}^s$, and $(\Delta H_f)_I^s - (\Delta H_f)_{II}^0$ calculated from eq 2–6 derived in the preceding section. Examination of the table reveals that the values of $(\Delta H_f)_I^s - (\Delta H_f)_I^{CCl_4}$ determined by means of the hydrazobenzene reaction and by means of the 4-*t*-butylphenol reaction are in agreement within the error limits of the measurements required for their calculation.

Effect of Solvent on $(\Delta H_f)_I^s$. The transfer of the 2,4,6-tri-*t*-butylphenoxy radical from a state of infinite dilution in carbon tetrachloride or chlorobenzene to a state of infinite dilution in benzene corresponds to an enthalpy change of *ca.* +1.3 kcal/mol. Other solvent systems manifest somewhat smaller endothermicities. These rather small effects are best analyzed by a direct comparison of the solvent effects on the radical with the corresponding hydrocarbon, 1,3,5-tri-*t*-butylbenzene (V).

Table IV. A Summary of Data for the Calorimetric Study of the 2,4,6-Tri-*t*-butylphenoxy Radical in Solution at 298°K

Reactant	Solvent	$(\Delta H_{\text{obsd}})^{s}$, kcal/mol	$(\Delta H_f)_I^s - (\Delta H_f)_I^{CCl_4}$, kcal/mol	$(\Delta H_f)_I^s - (\Delta H_f)_{II}$, kcal/mol	$(\Delta H_f)_I^s - (\Delta H_f)_{II}^{\circ}$,[d] kcal/mol
	CCl_4	-27.40 ± 0.22		$+28.13 \pm 0.12$	$+30.74 \pm 0.20$
	C_6H_6	-29.56 ± 0.04	$+1.50 \pm 0.36$	$+29.14 \pm 0.08$	32.29 ± 0.20
	C_6H_5Cl	-28.00 ± 0.11	-0.30 ± 0.37	$+28.25 \pm 0.08$	30.45 ± 0.16
	C_6H_5Cl-tetralin[a]	-28.92 ± 0.10	-0.22 ± 0.29	$+28.91 \pm 0.05$	31.06 ± 0.09
	CCl_4-$C_4H_8O_2$[b]	-30.31 ± 0.10	$+0.81 \pm 0.32$	$+29.73 \pm 0.07$	31.55 ± 0.12
	CCl_4-CH_3CN[c]	-28.25 ± 0.36	$+0.95 \pm 0.50$	$+28.91 \pm 0.21$	31.74 ± 0.30
	CCl_4	-13.84 ± 0.17			
	C_6H_6	-15.07 ± 0.27	$+1.11 \pm 0.39$		
	C_6H_5Cl	-14.22 ± 0.15	-0.14 ± 0.23		

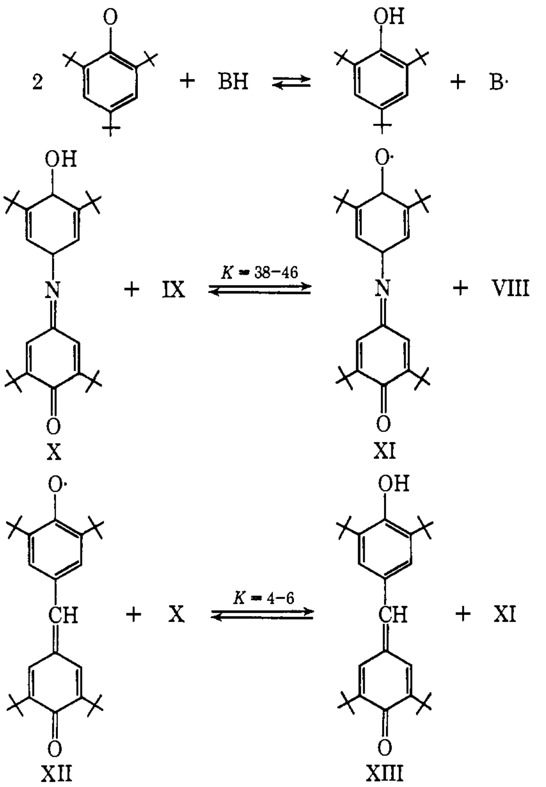
[a] Mole fraction of tetralin equal to 0.3350. [b] Mole fraction of dioxane equal to 0.5317. [c] Mole fraction of acetonitrile equal to 0.6486. [d] The absolute value of $(\Delta H_f)_I^s$ equals -113.1 ± 0.9 kcal/mol plus the value of this quantity.



V

In Figure 2 is presented a plot of $(\Delta H_f)_I^s$ *vs.* $(\Delta H_{\text{solution}})_V^s$.[8] If the solvent interactions with the hydrocarbon and the radical are exactly the same these quantities will be linearly related and a line drawn through the points will have a unit slope. As we see such a line does fit the data moderately well. Thus there appear only small specific solvent interactions (± 0.5 kcal/mol) with the radical due to its free electron and moreover the parent hydrocarbon serves as a good model for the solution properties of the free radical.[9]

Derived Values of Bond Energies of Other Stable Free Radicals. There have been several systems in which the equilibrium constants and/or heats of reaction have been determined for the reactions where **B**· is a second "stable" free radical. Cook, *et al.*,[10] reported values of *K* equal to 51.7 ± 4.1 and ΔH equal to -3.42 ± 0.17 kcal/mol where BH is 2,6-di-*t*-butyl-4-*t*-butoxyphenol (VI) and B· is 2,6-di-*t*-butyl-4-*t*-butoxyphenoxy (VII) in benzene at 25°. Ayscough and Russell[11] reported values of *K* equal to 10 ± 3 and ΔH equal to -1.6 ± 0.3 kcal/mol where BH is diphenylpicrylhydrazine (VIII) and B· is the diphenylpicrylhydrazyl free radical (IX) in benzene at 20°. The equilibrium constants for the exchange reactions have recently been determined by Bartlett and Purrington[12] at 25° in benzene solution.



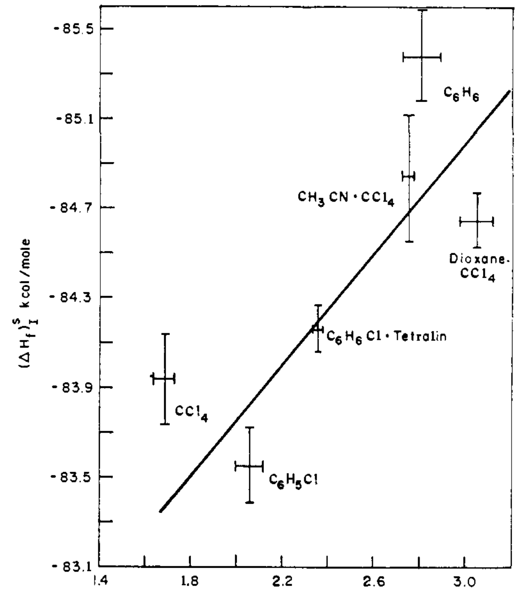


Figure 2. Comparison of the effect of solvent upon the values of $(H_f)_i^s$ for I and V.

We are now in a position to estimate the differences in the heats of formation of these free radicals and the molecules from which they are derived, $(\Delta H_f)_{B\cdot}^{\text{benzene}} - (\Delta H_f)_{BH}^{\text{benzene}}$, by combining the results of the equilibrium studies and the value of $(\Delta H_f)_I^{\text{benzene}}$ —

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(8) From eq 1 this quantity is equal to $(\Delta H_f)_{TTB}^s - (\Delta H_f)_{TTB}^{\circ}$.

(9) The melting points of the two solids are also similar: 96–98° for I[4] and 73.0–73.3° for IV. The small differences in the solution properties may be due to dipole–solvent interactions; compare the values of $(\Delta H_{\text{solution}})_{III}^s$, Table II, which increase in the order $C_6H_5Cl < CCl_4 < C_6H_6$.

(10) C. D. Cook, C. B. Depatic, and E. S. English, *J. Org. Chem.*, **24**, 1356 (1959).

(11) P. B. Ayscough and K. E. Russell, *Can. J. Chem.*, 43, 3039 (1965).

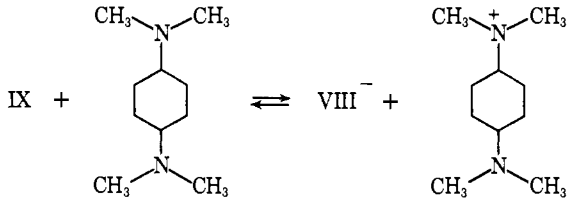
(12) P. D. Bartlett and S. T. Purrington, *J. Am. Chem. Soc.*, **88**, 3303 (1966).

Table V. Summary of Values of $(\Delta H_f)_{B\cdot}^{benzene} - (\Delta H_f)_{BH}^{benzene}$ for Stable Radicals in Benzene at 298°K

B· radical	BH molecule	$(\Delta H_f)_{B\cdot}^{benzene} - (\Delta H_f)_{BH}^{benzene}$, kcal/mole
I	II	29.14 ± 0.08
IX	VIII	27.5 ± 0.4
XII	XIII	26.4 ± 0.5[a]
VII	VI	25.72 ± 0.25
XI	X	25.6 ± 0.5[a]

[a] Calculated assuming that ΔS for the hydrogen-atom transfer equilibrium is negligible as is the case for the VI–VII[10] and VIII–IX[11] system.

$(\Delta H_f)_{II}^{benzene}$, determined in the present work. In Table V are summarized the values of $(\Delta H_f)_{B\cdot}^{benzene} - (\Delta H_f)_{BH}^{benzene}$. This approach, *i.e.*, direct equilibrium studies, should prove satisfactory for systems in which the molecule BH possesses a bond energy approximately equal to or smaller than the bond energy for II and therefore yields the stable radical free radical B·. Enthalpy relationships between relatively stable cation radicals and the molecules from which they are derived may also be obtained by such equilibrium techniques. For example, Hausser[13] has reported a reversible electron transfer reaction between the diphenylpicrylhydrazyl free radical, (IX) and N,N′-tetramethyl-*p*-phenylenediamine, *i.e.*

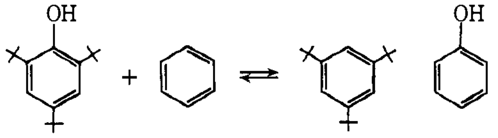


with a heat of reaction in toluene at −40° equal to −20 ± 5 kcal/mol.

For systems where the bond energy of BH is significantly higher than II, *i.e.*, hydroperoxides and phenols, and therefore yield more reactive radicals, kinetic studies of the rates of the hydrogen abstraction reaction in both directions are necessary. Studies of these types involving hydroperoxide–peroxy radical systems are now in progress and will be the subject of future reports from this laboratory.

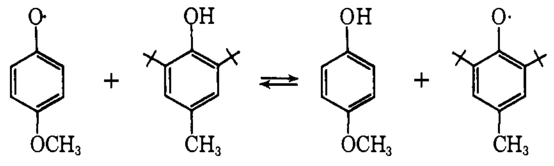
Strain Energy in 2,4,6-Tri-*t*-butylphenol. Arnett, *et al.*,[14] have recently demonstrated that the strain energy in 1,2-di-*t*-butylbenzene systems amounts to 22 kcal/mol. It is reasonable that considerable strain should be associated with the 2,6-di-*t*-butylphenol group. This strain would then be partially relieved upon the loss of a hydrogen atom[15] to form the corresponding 2,6-di-*t*-butylphenol radical and the O–H bond energy of the molecule would have an abnormally low value.[16,17]

A quantitative estimate of the strain energy in 2,4,6-tri-*t*-butylphenol compared to simple phenols may be made by means of the following analysis. Consider the hypothetical reaction



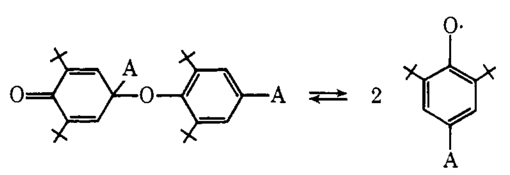
in the gas phase at 298°K. Utilizing the recently determined heat of formation of 1,3,5-tri-*t*-butylbenzene[18] and 2,4,6-tri-*t*-butylphenol,[7] the heats of sublimation of these compounds,[19] and the known heats of formation in the gas phase of benzene and phenol,[20] the heat of the reaction is calculated as equal to −8.0 ± 2.0 kcal/mol. This steric strain energy is unique to the *t*-butyl group since the heats of the reactions of benzene with 2-methylphenol and 2,6-dimethylphenol to yield phenol and the corresponding hydrocarbons are equal to 0 ± 0.5 kcal/mol.

The strain energy associated with 2,6-di-*t*-butylphenol systems compared to nonhindered phenols accounts for the synergistic behavior as antioxidants manifested by mixtures of the two classes of compounds. One of the key features of the mechanism recently proposed by the present authors[2] for this type of synergism involves the favorable position of the hydrogen atom transfer equilibrium



The partial relief of strain energy in the hindered phenol upon the formation of the hindered phenoxy radical thus provides a strong driving force for the equilibrium to lie to the right.[21]

This strain energy manifests itself in other unique properties associated with 2,6-di-*t*-butylphenoxy systems. Williams and Kreilick[22] have recently measured the heat of dissociation in solution of the dimers derived from 2,6-di-*t*-butylphenoxy-4- substituted radicals, *i.e.*



The decrease in the heat of the dissociation reaction with increasing bulk of A and the extremely low values of these heats, 6–12 kcal/mol, are no doubt due to the relief upon dissociation of the strain energy of the dimer

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(13) K. H. Hausser, *Naturwissenschaften*, **46**, 597 (1959).

(14) E. M. Arnett, J. C. Sanda, J. M. Bollinger, and M. Barber, *J. Am. Chem. Soc.*, **89**, 5389 (1967).

(15) The rotation of the OH group in 2,4,6-tri-*t*-butylphenol is severely hindered; *cf.* M. Davis and L. Meakins, *J. Chem. Phys.*, **26**, 1584 (1956). In contrast the *o*·*t*-butyl groups of the radical are freely rotating at room temperature. *Cf.* K. Mukai, N. Hishiguchi, K. Ishizu, Y. Deguchi, and H. Takaki, *Bull. Chem. Soc. Japan*, **40**, 2731 (1967).

(16) Although a value of the O–H bond energy of II in the gas phase equal to *ca.* 80 kcal/mol may be calculated upon the assumption that $[(\Delta H_f)_I^{gas} - (\Delta H_f)_I^{CCl_4}]$ is equal to $[(\Delta H_f)_V^{gas} - (\Delta H_f)_V^{CCl_4}]$, a referee has correctly pointed out that this assumption requires that the quantity $[(\Delta H_{sublimation})_I - (\Delta H_{solution})_I^{CCl_4}]$ be equal to $[(\Delta H_{sublimation})_V - (\Delta H_{solution})_V^{CCl_4}]$. At present there are insufficient thermodynamic data for solid II to test the validity of the assumption.

(17) A value of the O–H band energy of simple phenol equal to 90 ± 2 kcal/mol has been suggested; *cf.* S. W. Benson, *J. Am. Chem. Soc.*, 87, 972 (1965).

(18) U. Kruerke, C. Hoogzand, and W. Hubel, *Chem. Ber.*, **94**, 2817 (1961).

(19) M. Davies and B. Kybett, *Trans. Faraday Soc.*, **61**, 1608 (1965).

(20) R. J. L. Andon, D. P. Biddiscombe, J. D. Cox, R. Handley, D. Harrod, E. F. Herington, and J. F. Martin, *J. Chem. Soc.*, 5246 (1960).

(21) In aromatic solvents, *i.e.*, benzene, an additional −1.5 kcal is added to the heat of the reaction due to the more favorable OH bond solvation with benzene of the nonhindered phenol; *cf.* Table II.

(22) D. J. Williams and R. Kreilick, *J. Am. Chem. Soc.*, 90, 2775 (1968).

due to 2,6-di-*t*-butylphenoxy interactions with A. When A is an alkyl group, the stability of the dimer also decreases with the size of the alkyl substituent. Thus the dimer of 2,6-di-*t*-butyl-4-methylphenoxy can be isolated.[23] In contrast there is no evidence for the formation of the dimers of 2,6-di-*t*-butyl-4-isopropyl- or -4-cyclohexylphenoxy[5] and the 4-*t*-butyl[4] and the 4-phenyl compounds[24] have clearly been demonstrated to be monomeric in solution.

Experimental Section

Materials and Solvents. Preparation of 4-(4-*t*-butylphenoxy)-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one (IV) was previously described.[3] Hydrazobenzene was prepared from *trans*-azobenzene according to the procedure of Corey, *et al.*[25] The other compounds utilized in the present work were obtained from commercial sources and were purified by recrystallization to yield materials whose melting points agreed with the literature values.

Benzene and carbon tetrachloride were spectroquality reagent grade (Matheson Coleman and Bell). The chlorobenzene was "Baker Analyzed" reagent grade which was passed through a column of activated alumina before use. Tetralin (Aldrich) was purified by the procedure previously described.[26] Immediately prior to use it was passed through an activated alumina column under nitrogen. Spectroquality acetonitrile (Matheson Coleman and Bell) was refluxed over and distilled from phosphorus pentoxide and then distilled from fused sodium carbonate. Spectroquality dioxane was refluxed over and distilled from sodium metal under nitrogen.

Preparation of 2,4,6-Tri-*t*-butylphenoxy Radical. A 0.5 *M* solution of 2,4,6-tri-*t*-butylphenol in carbon tetrachloride, benzene, or chlorobenzene was shaken successively with a 0.2 *M* sodium hydroxide solution saturated with potassium ferricyanide (three times) and a saturated sodium chloride solution (once) under argon. The two layers were separated, and the radical solution was dried by passing it through a column of Celite (503) and anhydrous sodium sulfate (1:1) into a reservoir. For the studies in mixed solvents, solutions of the radical were prepared in pure carbon tetrachloride or chlorobenzene and subsequently diluted with either dioxane, acetonitrile, or tetralin. Solutions of the radical could be kept for several hours under argon with little loss in concentration.

Analysis for *trans*-Azobenzene. A solution of 2,4,6-tri-*t*-butylphenoxy radical (*ca.* 0.2 *M*) was prepared and *ca.* 40 ml was transferred under argon to a tared flask. A 5-ml aliquot of this solution was added to 15 ml of a 0.25 *M* solution of 2,6-di-*t*-butylphenol in the same solvent. The resulting pale yellow solution was set aside to be used subsequently as blank for the spectral measurements. The remaining radical solution was weighed and the volume calculated from the solvent density. To that solution was added a less than stoichiometric amount (50–100 mg) of hydrazobenzene *via* a sample injection syringe in a plastic bag (*cf.* below). After stirring for 5 min a 6-ml aliquot was removed and added to 15 ml of 0.25 *M* 2,6-di-*t*-butylphenol solution. The resulting solution was a dark orange. All of these operations were carried out under argon and in a room illuminated by an infrared heating lamp to prevent any *trans* to *cis* photoisomerization of azobenzene. The spectra of a diluted sample of the quenched radical–hydrazobenzene solution was then measured at least twice from 4000 to 5000 Å. The duplicate spectra were indistinguishable from the original and were superimposable with the spectra of *trans*-azobenzene. The yield of *trans*-azobenzene based upon hydrazobenzene reacted reported in Table I was calculated from the extinction coefficient of *trans*-azobenzene at its maximum absorption. The position of the maximum absorption and the extinction coefficient (M^{-1} cm^{-1}) as a function of solvent determined for *trans*-azobenzene are shown in Table VI. The extinction coefficient for quinol ethers in this region, *i.e.*, IV, is 2–3 M^{-1} cm^{-1}.

Table VI

Solvent	λ_{max}, Å	ϵ, M^{-1} cm^{-1}
CCl_4	4450	478 ± 2
C_6H_6	4480	494 ± 2
C_6H_5Cl	4450	478 ± 2
CH_3CN–CCl_4	4450	498 ± 2
$C_4H_4O_2$–CCl_4	4470	491 ± 2

Calorimetry. The calorimeter with base line compensator and sample injection assembly was essentially that recently described by Arnett, *et al.*,[27] except that an adjustable-speed, constant-voltage magnetic stirrer with a Teflon-coated stirring bar was used. This particular arrangement allowed the calorimeter and sample injection unit to be enclosed in a plastic bag under an argon atmosphere. The plastic bag was flexible enough to allow easy external handling of the sample syringe. The heat of solution of KCl in water at 25° was found to be equal to 4.20 ± 0.04 kcal/mol (lit.[28] 4.185 ± 0.007 kcal/mol).

A minimum of three determinations of the partial molar enthalpy of solution at infinite dilution were made for each compound reported in the present study. Plots of the calories absorbed *vs.* moles of compound dissolved were linear with essentially zero intercepts. The data were treated by the method of least squares and the reported uncertainties represent standard deviations from the mean. The values of the partial molal enthalpies of solution at infinite dilution for II and for azobenzene were not altered by the presence of the 2,4,6-tri-*t*-butylphenoxy radical in the solvent (*cf.* Table II).

For the determination of the heats of reaction of the 2,4,6-tri-*t*-butylphenoxy radical (I) with hydrazobenzene or 4-*t*-butylphenol a concentrated solution of the radical (0.2–0.5 *M*) was prepared as described above. Two hundred milliliters of the radical solution was placed in the calorimeter which had been previously flushed with argon and the entire assembly was enclosed in a plastic bag and flushed with argon. After two heat calibrations, a weighed sample of hydrazobenzene or 4-*t*-butylphenol (50–300 mg) was introduced into the solution by means of the solid sample syringe. The total time of heat evolution and reestablishment of the base line was *ca.* 20 sec. Two further heat calibrations were made and the results were calculated from the chart recordings. For the experiments reported in Table III, the concentration of the radical solution was determined by withdrawing 5 ml of the contents of the calorimeter (originally 205 ml for these experiments), injecting the aliquot into a solution of excess hydrazobenzene, and determining the amount of azobenzene formed in the reaction. Blank experiments revealed that the manipulation of the sample syringe did not result in any detectable evolution or absorption of heat when the calorimeter contained pure solvent or a solution of I in the solvent.

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[27] E. M. Arnett, N. G. Bentrude, J. J. Burke, and P. McC. Duggleby, *ibid.*, **87**, 1541 (1965).

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