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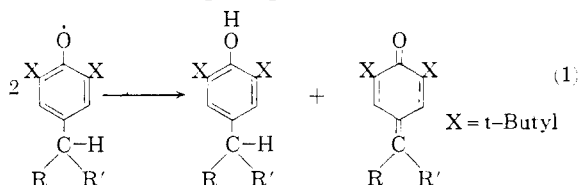
## Oxidation of Hindered Phenols. VII. Solvent Effects on the Disproportionation of Certain Phenoxy Radicals

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The 2,6-di-*t*-butyl-4-isopropyl-, 4-cyclohexyl- and 4-*sec*-butylphenoxy radicals disproportionate to the corresponding quinone methides and the parent phenols by reactions second order in phenoxy radical. In benzene the enthalpies of activation increase in the order isopropyl, *sec*-butyl and cyclohexyl. The enthalpies of activation for 2,6-di-*t*-butyl-4-isopropylphenoxy vary from 4.91 to 7.57 kcal./mole over a range of solvents, increasing as the dielectric constant of the solvent increases. Compensating changes in entropy of activation (in the range -30 to -40 e.u.) result in reaction rates which are relatively insensitive to changes in media over the temperature range studied. These results closely parallel the solvent effects found in a study of the decomposition of phenylazotriphenylmethane.<sup>1</sup> In the present case the regular dependence of enthalpy of activation upon dielectric constant strongly suggests that the solvent effects in this reaction are to be attributed primarily to dipolar interactions between the radicals and the solvent.

Recently there has been interest in solvent effects upon radical reactions.<sup>1-4</sup> The disproportionation of 2,6-di-*t*-butyl-4-*sec*-alkylphenoxy radicals to produce quinone methides and regenerate the parent phenols (eq. 1) appeared to be an excellent system for such a study since it has been shown<sup>5</sup> to give good second-order kinetics



and could be conveniently followed by spectrophotometric means. Since these radicals must have considerable dipolar character and since their highly hindered nature should minimize specific, close-range interactions, it was hoped that the results might be particularly amenable to theoretical analysis. Despite the fact that experimental limitations proved to be greater than originally anticipated, this expectation met with a reasonable degree of success.

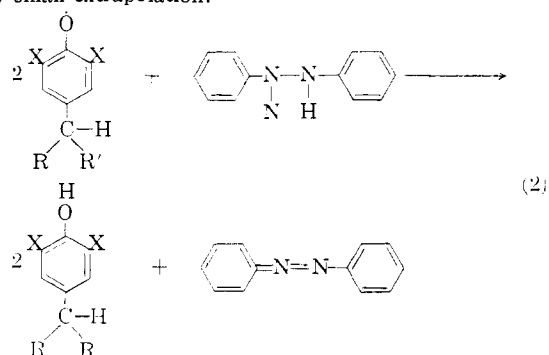
Rates were measured by oxidizing carefully degassed solutions of the phenols with oxygen-free alkaline ferricyanide solution in an evacuated reaction vessel (Fig. 1), transferring the resulting radical solutions to a spectrometer cell and following the decrease in optical density at 630 m $\mu$ . Extinction coefficients were determined by quenching the radical solutions with hydrazobenzene and then spectrometrically determining the azobenzene produced<sup>6</sup> (eq. 2).

## Experimental

**Determination of Extinction Coefficients.**—A solution (0.01 *M*) of the phenol in the appropriate solvent was

- (1) M. C. Alder and J. E. Leffler, *THIS JOURNAL*, **76**, 1425 (1954).
- (2) G. A. Russell, *ibid.*, **79**, 2977 (1957).
- (3) M. D. Cohen, J. E. Leffler and L. M. Barbato, *ibid.*, **76**, 4169 (1954).
- (4) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).
- (5) C. D. Cook and B. E. Norcross, *THIS JOURNAL*, **78**, 3797 (1956).
- (6) It is of interest to note that in this oxidation *trans*-azobenzene is first produced. Evidence for this comes from the fact that in the spectrometer beam, the optical density rose rapidly during the first few minutes of exposure. Since *cis*-azobenzene has extinction coefficients appreciably larger than *trans*-azobenzene,<sup>7</sup> the increase in optical density undoubtedly is due to the photoinitiated isomerization of the *trans* form to the *cis* form.
- (7) A. H. Cook, D. G. Jones and J. B. Polya, *J. Chem. Soc.*, 1315 (1939).

placed in bulb A of the Pyrex vacuum cell shown in Fig. 1. After outgassing by four alternate freezings and thaws under vacuum, the apparatus was sealed at B at a pressure of not more than 0.05 mm. When the assembly had come to room temperature, the ball joint C, containing an ampule of degassed ferricyanide solution (0.1 *M* sodium hydroxide solution saturated with potassium ferricyanide), was rotated to break the tip of the ampule. The mixture in bulb A was gently swirled until visual observation indicated the desired radical concentration and the radical solution carefully decanted through the gauze plug (which served to dry the solution) into the spectrometer cell. After noting the volume of solution as indicated by the calibrations on F, the optical density at 630 m $\mu$  was determined on a Beckman model DK-1 recording spectrometer. (Since the phenoxy radicals have very broad maxima at about 630 m $\mu$ , all of the extinction coefficients were determined at this wave length.) At the instant the optical density was recorded, a timer was started. Ball joint D was then rotated to break the ampule containing the quench solution, a degassed 0.01 *M* solution of hydrazobenzene in the same solvent. The total volume of the solution was determined by the calibration at G. The time lapse between the measurement of the optical density and the disappearance of the last trace of blue color was only about 10 seconds; thus the determination of the radical concentration at the moment of quenching involved only a very small extrapolation.



The spectrometer beam initiated *trans*-*cis* isomerism of the azobenzene<sup>6</sup> and the time required for equilibration was too long for practical manipulation. It was, however, found practicable to rapidly bring about equilibration by exposure to a Hanovia light under standardized conditions. After this exposure the optical density was determined at the maximum (around 440 m $\mu$ ) for the particular solvent. Several repeat measurements were made to ensure that equilibration had actually been achieved. By using known solutions of azobenzene, the apparent extinction coefficients of the azobenzene were determined under the same conditions. From these data, the concentration of the phenoxy radical, and hence its extinction coefficient, could be determined. The extinction coefficient of 2,4,6-tri-*t*-butylphenoxy, a very stable radical,<sup>8,9</sup> was measured as a check on the method.

- (8) C. D. Cook and R. C. Woodworth, *THIS JOURNAL*, **75**, 6242 (1953).
- (9) C. D. Cook, D. A. Kuhn and P. Fianu, *ibid.*, **78**, 2002 (1956).

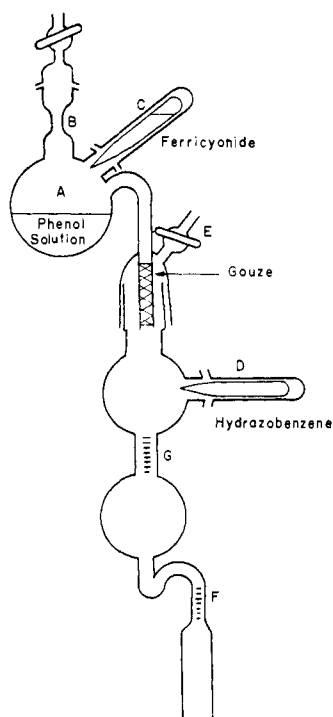


Fig. 1.—Apparatus for determination of extinction coefficients.

The value for the molar extinction coefficient in benzene was  $410 \pm 8$  which agrees very well with that of  $400 \pm 3$  determined by an entirely different method.<sup>10</sup> The molar extinction coefficients at  $630 \text{ m}\mu$  for 2,6-di-*t*-butyl-4-isopropylphenoxy in the different solvents were: benzene,  $404 \pm 8$ ; cyclohexane,  $462 \pm 18$ ; anisole,  $412 \pm 14$ ; chlorobenzene,  $467 \pm 15$ ; benzonitrile,  $450 \pm 11$ . All of these results are the average of at least eight runs. In cyclohexane, 2,4,6-tri-*t*-butylphenoxy gave a value of  $478 \pm 11$ , and 2,6-di-*t*-butyl-4-cyclohexylphenoxy gave values of 450 and 451 in two determinations. The lower bulbs in Fig. 1 are mixing chambers, and stopcock E was a means of breaking the vacuum in order to disassemble the apparatus. The reverse bend at F served to keep pieces of glass from the ampule out of the optical cell.

**Determination of Reaction Rates.**—In these determinations, the lower half of the apparatus pictured in Fig. 1 was replaced by a Pyrex cell attached directly to a standard taper joint. After degassing and equilibrating at the desired temperature, the radical was generated and decanted through the gauze plug into the optical cell. The assembly was rapidly transferred to the recording spectrometer which was equipped with a large, thermostated cabinet surrounding the cell compartment. The temperature of this cabinet was controlled to  $\pm 0.02^\circ$ . The wave length of spectrometer was set at  $630 \text{ m}\mu$  and the chart drive served to measure the time. Separate runs on a Beckman model DU spectrometer, where the cells were out of the light path for varying lengths of time, showed that the reaction was not subject to any photochemical effects at the wave length used. Rates were shown to be independent of the concentration of phenol and of quinone methide.

The general method worked very well for all solvents chosen except nitrobenzene. In view of the relationship found between the enthalpy of activation and the dielectric constant (see Discussion) data for this solvent were particularly desirable. Due apparently to mechanical difficulties (high solvent density and a tendency to emulsify) and a rather rapid reaction rate, it proved to be impossible to obtain reproducible data with this solvent. There also was some indication that a side reaction was occurring.

(10) C. D. Cook, C. B. Depatie and E. S. English, unpublished work. The technique involves the reaction of 2,4,6-tri-*t*-butyl-4-bromo-2,5-cyclohexadienone with mercury.

**Treatment of Data.**—Large scale plots of the reciprocals of optical density *vs.* time were usually excellent straight lines indicating the second-order nature of the reaction. This linearity pertained over at least 3 half-lives. Infrequently a plot deviated from linearity by curving downward. This was found to be due to droplets of the ferricyanide leaking through the gauze packing and settling on the surface of the cell. On the assumption that these droplets remain of constant size and shape during the course of a run, it can easily be shown that in such cases a constant value should be subtracted from the optical densities before taking the reciprocals. When empirically determined constants were used with such data, in every case the lines became straight and the slopes approached those of reactions which needed no correction. By deliberately introducing ferricyanide into the cells it was shown that the rate of oxidation of the phenol when controlled by diffusion was far too slow to create any error. As a consequence, such data were utilized in a few cases, but in all series the bulk of the data required no correction. These results also indicate that dissolved water has little if any effect upon the rate; the gauze was generally remarkably effective in drying the solutions. Thus the samples which were run at 50 and  $55^\circ$  generally had cloud points well below room temperature but these runs had the same rate as those which contained droplets of ferricyanide and hence are presumed to be nearly saturated with water.

Activation energies and enthalpies and entropies of activation were determined in the usual way, using the root-mean square method. Figure 2 shows a typical rate plot and a corrected run; Fig. 3 shows typical Arrhenius plots.

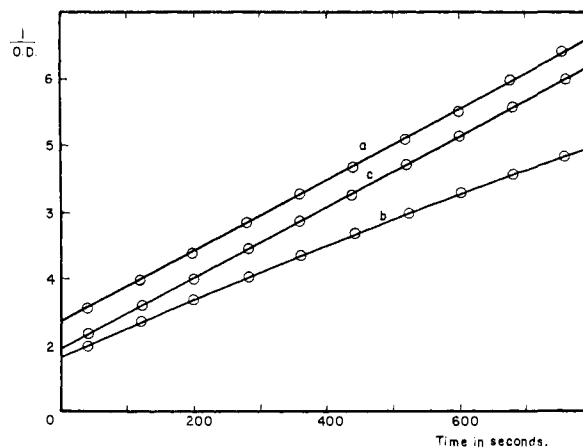


Fig. 2.—Rate curves for disproportionation of 2,6-di-*t*-butyl-4-isopropylphenoxy in benzene at  $25^\circ$ : a, run 1, uncorrected; b, run 2, uncorrected; c, run 2, corrected by subtraction of an empirically derived constant of 0.040 from the optical density.

**Preparation of Compounds.** 2,6-Di-*t*-butyl-4-cyclohexylphenol.<sup>11</sup> Thirty grams of *p*-cyclohexylphenol<sup>12</sup> and 2 ml. of concentrated sulfuric acid were dissolved in 30 ml. of benzene and isobutylene bubbled through the system at  $80^\circ$  until a weight gain of 21 g. (10% mole excess) was achieved. The reaction mixture was diluted with benzene, washed with water and sodium hydroxide solution and the benzene removed. After one recrystallization, yields of 70–80% were realized. The material showed an interesting melting point behavior; freshly prepared material melted at  $114\text{--}115^\circ$  but after standing a few days it melted at the reported<sup>13</sup> value of  $98\text{--}99^\circ$ . The lower melting form would usually resolidify in the melting point tube if heated for a few minutes at about  $100\text{--}110^\circ$  and the resolidified material would then melt at  $114\text{--}115^\circ$ . If the molten material at  $99\text{--}100^\circ$  was quickly cooled it then would partially melt at about  $75^\circ$ , resolidify below  $95^\circ$  and again melt at  $98\text{--}99^\circ$ .

(11) Work by Mr. John B. Lounsbury.

(12) Provided through the courtesy of Dr. Gilbert Theisen, Koppers Chemical Co.

(13) G. H. Stillson, D. W. Sawyer and C. K. Hunt, *THIS JOURNAL*, **67**, 303 (1945).

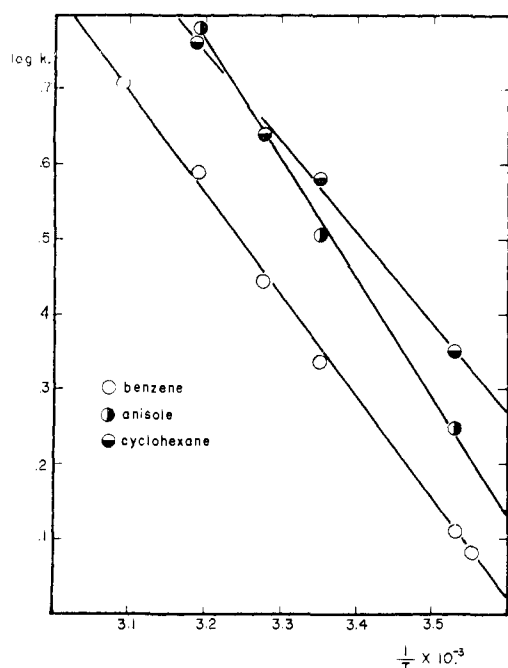


Fig. 3.—Typical Arrhenius plots for the disproportionation of 2,6-di-*t*-butyl-4-isopropylphenoxy in different solvents.

**Preparation of 2,6-Di-*t*-butyl-4-ethylphenol.**—This phenol was prepared from *p*-ethylphenol in 60–70% by the method previously reported<sup>14</sup> for 2,4,6-tri-*t*-butylphenol. After several recrystallizations from ethanol-water the product melted at 43.5–45°, reported<sup>13</sup> 44°. <sup>13</sup>

**Preparation of 2,6-Di-*t*-butyl-4-ethenyl Quinone Methide.**—A solution of 20 g. of 2,6-di-*t*-butyl-4-ethylphenol in 50 ml. of benzene was stirred under a nitrogen atmosphere with an excess of alkaline ferricyanide solution until the blue color of the phenoxy radical disappeared. The product, obtained in 80–85% yield after one recrystallization from *n*-hexane, melted at 92–93.5°. Calcd. for C<sub>16</sub>H<sub>22</sub>O: C, 82.70; H, 10.41. Found: C, 83.03; H, 10.53.

### Discussion

Rate constants for the disproportionation of the phenoxy radicals in benzene are listed in Table I. Since the determination of extinction coefficients

TABLE I  
RATES OF DISPROPORTION IN BENZENE

<i>T</i> , °C.	I. m. <sup>-1</sup> sec. <sup>-1</sup>		
	2,6-Di- <i>t</i> -butyl-4-isopropylphenoxy	2,6-Di- <i>t</i> -butyl-4- <i>sec</i> -butylphenoxy	2,6-Di- <i>t</i> -butyl-4-cyclohexylphenoxy
8.00	1.21 ± 0.05		
10.00	1.30 ± .05		0.597 ± 0.03 <sup>a</sup>
25.00	2.17 ± .01	0.618 ± 0.015 <sup>a</sup>	1.28 ± .02 <sup>a</sup>
32.00	2.78 ± .04		
40.00	3.87 ± .04	1.12 ± .01 <sup>a</sup>	2.31 ± .03 <sup>a</sup>
50.00	5.10 ± .02		
55.00		2.11 ± .01 <sup>a</sup>	

<sup>a</sup> Estimated assuming radical has same extinction coefficient as 2,6-di-*t*-butyl-4-isopropylphenoxy.

was a very laborious process and since the absolute concentrations were unnecessary for the determination of activation energies, it was assumed that the extinction coefficients were essentially the same for all three radicals. The extinction coefficient data listed under Experimental indicate this is a safe assumption; it appears certain that the dif-

ferences in rate constants between the radicals are far greater than any difference in extinction coefficients.

Attempts were made to measure the rates of disappearance of 2,6-di-*t*-butyl-4-methylphenoxy and 2,6-di-*t*-butyl-4-ethylphenoxy. The first of these is of particular interest because the measurements might shed some light on its apparent rearrangement and dimerization to 4,4'-di-hydroxy-3,5,3'5'-tetra-*t*-butyl-1,2-diphenylethane.<sup>15</sup> Unfortunately, even at the lowest practical temperature (~6°) the rate of disappearance of 2,6-di-*t*-butyl-4-methylphenoxy is much too fast to measure by the present technique. The -4-ethylphenoxy radical reacts appreciably more slowly but is still too fast for accurate measurement. At 25° the rates decrease with substituent in the 4-position in the order methyl > ethyl > isopropyl > cyclohexyl > *sec*-butyl. While this is about the order expected on a basis of steric hindrance, Table III shows that any such generalization must be made with caution since the activation energies increase in the order isopropyl < *sec*-butyl < cyclohexyl.

Table II lists the rates of disproportionation of 2,6-di-*t*-butyl-4-isopropylphenoxy in a variety of solvents, and Table III gives the activation parameters derived from these data. It is to be noted that the reaction is characterized by a large negative entropy of activation and a low enthalpy of activation.

Leffler<sup>1</sup> has recently emphasized the fact that the apparent indifference in the rates of many radical reactions to changes in solvent may be due to compensating changes in the entropy and enthalpy of activation rather than to any lack of interaction with the solvent. The present work provides another example of such a compensating trend as can be seen from Table III or by examination of the isokinetic plot (Fig. 4). The latter shows the frequently observed<sup>4</sup> linear relationship between the enthalpy and the entropy of activation. The

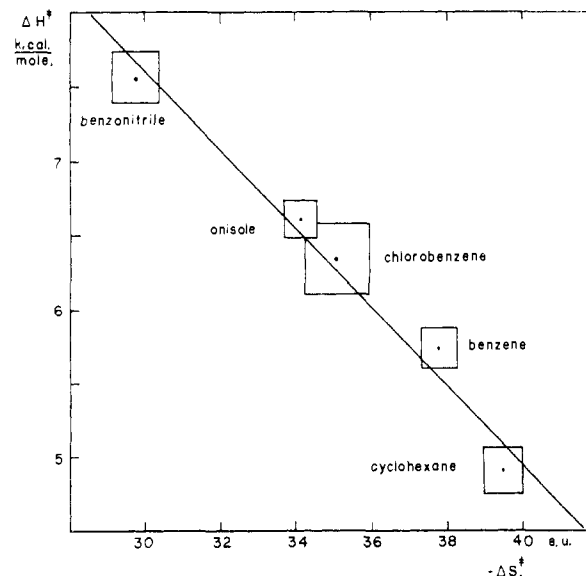


Fig. 4.—Isokinetic relationship.

(15) C. D. Cook, N. G. Nash and H. R. Flanagan, *THIS JOURNAL*, **77**, 1783 (1955).

(14) B. C. Somers and C. D. Cook, *J. Chem. Ed.*, **32**, 312 (1955).

TABLE II  
 RATES OF DISPROPORTIONATION OF 2,6-DI-*t*-BUTYL-4-ISOPROPYLPHENOXY IN DIFFERENT SOLVENTS

<i>T</i> , °C.	Cyclohexane <sup>a</sup>	Chlorobenzene <sup>a</sup>	Anisole <sup>a</sup>	Solvent Benzonitrile <sup>a</sup>	Bromobenzene <sup>b</sup>	CCl <sub>4</sub> <sup>b</sup>
10.00	2.25 ± 0.02	1.57 ± 0.02	1.77 ± 0.02	2.53 ± 0.05	0.00370 ± 0.00001	0.003621 ± 0.00006
10.80	2.28					
25.00	3.82 ± .09	3.08 ± .08	3.20 ± .03	5.64 ± .07	.00756 ± .00004	.005625
30.00				6.16 ± .04		
32.00	4.37 ± .03					
35.00				8.23 ± .07	.010006 ± .00007	.00825 ± .00023
40.00		5.28 ± .02	6.10 ± .10			
40.50	5.81 ± .08	5.22 ± .15				
45.00						.01165 ± .00006

<sup>a</sup> Units of l. moles<sup>-1</sup> sec.<sup>-1</sup>. <sup>b</sup> Slope of plots of reciprocal of optical density vs. time in seconds.

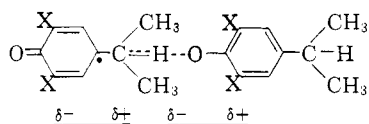
 TABLE III  
 ACTIVATION PARAMETERS

Radical, 2,6-Di- <i>t</i> -butyl-	Solvent	Activation energy $\Delta E_a$ , kcal./mole	Enthalpy of act. $\Delta H^\ddagger$ , 25° kcal./mole	Entropy of activation $\Delta S^\ddagger$ , cal./°/mole
Isopropylphenoxy	Benzene	6.23 ± 0.15	5.74 ± 0.14	-37.80 ± 0.50
	Cyclohexane	5.50 ± .18	4.91 ± .16	-39.46 ± .59
	Anisole	7.20 ± .14	6.61 ± .13	-34.12 ± .46
	Benzonitrile	8.16 ± .19	7.57 ± .17	-29.76 ± .63
	Bromobenzene	7.35 ± .11	6.76 ± .10	
	Chlorobenzene	6.94 ± .25	6.35 ± .23	-35.06 ± .82
<i>sec</i> -Butylphenoxy	Carbon tetrachloride	5.80 ± .09	5.21 ± .08	
	Benzene	7.04 ± .11	6.45 ± .10	
	Cyclohexylphenoxy	7.93 ± .14	7.34 ± .13	
	Cyclohexane	7.45 ± .11	6.83 ± .10	

slope of this line yields an isokinetic temperature of -9° where, if the relationship pertained precisely, all of the rates would be equal.

In general, two approaches have been taken to the interpretation of solvent effects on reaction rates. One is the essentially qualitative consideration of the relative degree of solvation of the reactants and the transition state. While still highly speculative, such discussions frequently lead to satisfactory rationalizations of the data. The alternative approach is to consider the interaction of the reactants as occurring in a continuous medium of the appropriate dielectric constant. While this gross approximation is rather unsatisfying, the method does provide the opportunity to treat the data mathematically. It is of interest to examine the present data from both points of view.

Based on the reaction products, the second-order kinetics and the polar nature of the radical, a reasonable model for the transition state would be a heads-to-tails complex as



Construction of models suggests that the most reasonable alternative, a head-to-tail, tail-to-head complex, is unlikely due to steric hindrance. While this possibility cannot be ruled out (particularly in the case of the 4-methyl compound) it does seem less likely than the above representation.

The data in Table III indicate that desolvation occurs as the radicals enter the transition state. Thus in a medium where the radicals are highly solvated, the enthalpy of activation would have to be relatively high to provide the necessary desolva-

tion energy and such cases would be accompanied by the largest entropy increases (or the smallest entropy decreases). The situation thus appears identical with the one described by Leffler<sup>1</sup> for the decomposition of phenylazotriphenylmethane. Table IV, comparing the enthalpies of activation obtained by Leffler with those of this work, shows a very definite parallel in the solvent effects on the two reactions. Solvent interaction with phenylazotriphenylmethane is apparently considerably greater than with the phenoxy radicals as can be seen by the greater differences in enthalpy of activation in the former case.<sup>16</sup> This can be explained on the basis that the relatively non-polar, bulky alkyl groups on the phenoxy radical prevent as strong an interaction between reactant and solvent as can occur with the unhindered azo compounds.

 TABLE IV  
 COMPARISON OF ENTHALPIES OF ACTIVATION IN VARIOUS SOLVENTS FOR THERMAL DECOMPOSITION OF PHENYLAZOTRIPHENYLMETHANE (LEFFLER<sup>1</sup>) AND THE DISPROPORTIONATION OF 2,6-DI-*t*-BUTYL-4-ISOPROPYLPHENOXY

Solvent	$\Delta H^\ddagger$ , kcal./mole	
	Leffler	This work
Cyclohexane	24.5 ± 0.1	4.91 ± 0.16
Benzene	26.8 ± .1	5.74 ± .14
Chlorobenzene	28.3 ± .1	6.35 ± .23
Anisole	28.3 ± 0.3; 28.8 ± 0.2	6.61 ± .13
Benzonitrile	29.0 ± 0.3	7.57 ± .17

The usual method of mathematically relating rates to the dielectric constant of the solvent is to calculate the changes in electrostatic energy of the reactants with changes of dielectric constant and

(16) It is, of course, also possible that more extensive desolvation is necessary in this case, although this seems less likely.

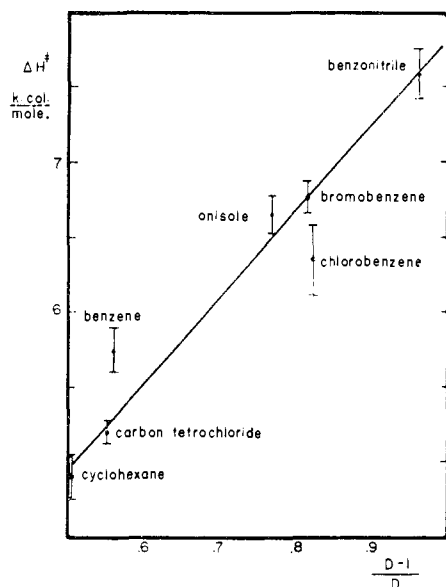


Fig. 5.—Activation enthalpy as a function of the dielectric constant of the medium.

to equate these to the changes in free energy of activation.<sup>17</sup> This technique has proved to be reasonably satisfactory for those cases where the dielectric constant is varied by changing the ratio of a mixture of solvents but has proved less satisfactory when going from one solvent to another. Further, it is obviously not applicable near the isokinetic temperature (or, perhaps, more correctly, isokinetic region) where the free energies of activation are nearly equal. In the present case, a casual inspection of the data which were taken very near to the isokinetic temperature shows that there is no direct relationship between the rate constants (and hence the free energies of activation) and the dielectric constants of the solvents. Further, it may be noted that if the temperature were appreciably higher or lower than the isokinetic temperature, the free energies of activation would vary in a regular way with the dielectric constants although the direction of variation would be opposite on the two sides of this temperature.

In isodielectric media, the difference in energy of alignment of two dipoles in a heads-to-tails orientation in two media of different dielectric constants is given by

$$\Delta E = \frac{-28.9 \mu_A \mu_B \Delta D}{D_1 D_2 r^3} \quad (3)$$

where  $\mu_A$  and  $\mu_B$  are the dipole moments,  $D_1$  and  $D_2$  are the dielectric constants of the media and  $r$  is the spacing between the dipoles.<sup>18</sup> Since the dielectric constants do not vary very much over the range of temperature used in this work, it is tempting to see if this expression will correlate the data. For this purpose it is convenient to put equation 3 in the form (4) where  $\Delta H_0^\ddagger$  is the enthalpy of acti-

vation in a medium of unit dielectric constant and  $\mu$  is the dipole moment of the radical. This equation predicts that a plot of  $\Delta H^\ddagger$  vs.  $(D-1)/D$  will be linear. Figure 5 is such a plot and while the agreement is by no means precise, it would be remarkable if it were purely fortuitous. As nearly as can be estimated from such a crude model, the slope of the line is of the correct order of magnitude. The relationship must, however, be taken as essentially empirical, since theoretically this development is tantamount to assuming that the entropy of activation remains constant.

$$\Delta H^\ddagger = \Delta H_0^\ddagger + \frac{28.9\mu^2(D-1)}{Dr^3} \quad (4)$$

The failure of  $\Delta F^\ddagger$  and the success of  $\Delta H^\ddagger$  to correlate with the dielectric constant are reminiscent of Leffler's<sup>4</sup> observation that near the isokinetic temperature enthalpies of activation show a better correlation with Hammett  $\sigma$ -values than do free energies of activation.

Similarly to our case, Leffler's data on phenylazotriphenylmethane<sup>1</sup> show that the free energy of activation varies in a capricious way with dielectric constant, but that the enthalpies of activation are roughly correlated by equation 4. In this case, closer interaction of the solvent dipole with that of the reactant is possible and it is to be expected that complications such as induced polarizations and specific steric effects would lead to rather large deviations from any direct relationship with dielectric constant. The structure of the phenoxy radicals minimizes such complications, and it is undoubtedly only for this reason that their behavior can be reasonably well correlated by so simple a relationship. The fact that they can be so correlated, however, once again emphasizes the fact that polar factors may play an important role in many free radical reactions.

The close parallelism in solvent effect between Leffler's study and the present work is particularly interesting in view of the fact that in the former case the reactant is a normal molecule which develops radical character on entering the transition state whereas in this instance the reactant is free radical in nature. A number of radical phenomena have recently been explained on a basis of complex formation between radicals and aromatic systems.<sup>2,19-21</sup> Such an explanation will not fit the data cited here since there is no correlation between the basicity of the solvent and the magnitude of the effect. In the cases where complexes have been postulated, the radicals have been much more strongly electrophilic in character than would be expected for a phenoxy radical.

**Acknowledgments.**—The authors are grateful to the National Science Foundation and the Research Corporation without whose support this work would have been impossible.

BURLINGTON, VT.

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(19) G. S. Hammond, *et al.*, *THIS JOURNAL*, **77**, 3238 (1955).

(20) F. R. Mayo, *ibid.*, **75**, 6133 (1953).

(21) R. A. Benkeser and W. Schroeder, *ibid.*, **80**, 3314 (1958).