tant in radical systems, a process of similar design may be responsible for the temperature dependence seen here.

In the reactant oxy radical, all bond angles are probably close to tetrahedral. As the reactant proceeds toward the transition state, the quaternary carbon of the reactant is being converted to an sp^2 carbonyl carbon. In the process, while carbon–carbon bond stretching occurs, the three bond angles that the α carbon of the departing group makes with each of the three groups bonded to the incipient carbonyl carbon approaches 90° and may result in hindering rotation of the methyl group of the departing ethyl. The frequencies of the torsions in the departing ethyl group associated with H_β–C_β–C_α–carbonyl C could thus be increased and result in counterbalancing the zero-point energy decrease associated with the decrease of the H_β–C_β stretching force constant.

References and Notes

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Kinetics and Mechanisms of the Reactions of Organic Cation Radicals and Dications. IV.[1] First- and Second-Order Reactions of Thianthrene Cation Radical with Phenol

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Abstract: The kinetics of the reaction between the thianthrene cation radical and phenol were studied in dichloromethane in the presence and absence of trifluoroacetic acid (TFA). In the presence of TFA, the reaction was found to be second order in $TH\cdot^{+}$, inhibited by unoxidized TH, first order in phenol, and the rate decreased markedly with increasing TFA concentration. The mechanism proposed for the reaction on the basis of the kinetics and comparison with other reactions of $TH\cdot^{+}$, which have previously been studied, involves initial complex formation between $TH\cdot^{+}$ and phenol followed by oxidation of the complex by $TH\cdot^{+}$. An altogether different picture emerged when the reaction was carried out in the absence of TFA. In the latter case, the reaction was found to be first order in both $TH\cdot^{+}$ and phenol, and the rate was independent of the concentration of unoxidized TH. The effect of TFA that brings about the abrupt mechanistic change is to suppress the deprotonation of the initial complex, which is accompanied by formation of a sulfur–carbon bond. In the presence of TFA, the deprotonation does not occur, and oxidation of the complex is necessary before bond formation takes place. The mechanistic conclusions are supported by comparing the reactions of $TH\cdot^{+}$ with phenol and anisole. In the latter case, the same mechanism holds both in the presence and absence of TFA since the acidic proton of phenol has been replaced by methyl.

The mechanism of the reaction of the thianthrene cation radical ($TH\cdot^{+}$) with anisole (AN) has recently been studied in detail[1b] and found to follow the following mechanism:

$$TH\cdot^{+} + AN \rightleftarrows (TH/AN)\cdot^{+} \tag{1}$$

$$(TH/AN)\cdot^{+} \rightleftarrows TH + AN\cdot^{+} \tag{2}$$

$$(TH/AN)\cdot^{+} + TH\cdot^{+} \rightleftarrows (TH/AN)^{2+} + TH \tag{3}$$

$$(TH/AN)^{2+} \rightarrow (TH\text{-}AN)^{+} + H^{+} \tag{4}$$

In both acetonitrile and dichloromethane, at low $TH\cdot^{+}$ concentration ($\sim 10^{-5}$ M), the only reaction observed was oxidation of AN via dissociation of the initial complex (step 2).

Table I. Pseudo-First-Order Reaction between $TH\cdot^{+}$ and PHOH[a]

Run no.	$[TH\cdot^{+}] \times 10^4$	$[TH] \times 10^4$	$[PHOH] \times 10^4$	k_{obsd}, s^{-1}	$k_{app} \times 10^{-2}$, s^{-1}[g]
1	0.30	8.80	5	0.28	5.6
2	0.46	8.73	5	0.25	5.0
3	0.91	7.83	5	0.24	4.8
4	0.91	8.01	5	0.27	5.4
46	1.06	8.43	5	0.13[b]	2.6
47	1.06	8.15	5	0.15[b]	3.0
48	1.06	8.30	5	0.16[b]	3.2
5	0.83	8.73	5	0.33[c]	6.6
6	1.52	8.25	5	0.28	5.6
7	1.21	16.7	5	0.21	4.2
8	0.99	27.7	5	0.20	4.0
9	1.06	28.4	5	0.26[c]	5.2
10	0.57	8.80	2	0.21	6.0
11	0.91	8.19	10	0.50	5.0
12	0.76	8.07	10	0.56	5.6
13	0.91	8.86	10	0.50[d]	5.0
14	0.30	8.95	10	0.69[e]	6.9
15	1.49	8.31	5	0.036[f]	0.72
16	0.45	10.0	5	0.041[f]	0.82
17	1.27	9.88	5	0.041[f]	0.82

[a] Solvent: CH_2Cl_2, $[n\text{-}Bu_4NBF_4] = 0.1$ M; temp 11°C; concentrations in mol/l. [b] Reaction with PhOD. [c] Temp 16°C. [d] [2,4,6-Trinitrophenol] = 10^{-3} M. [e] [2,4,6-Trinitrophenol] = 10^{-2} M. [f] Solvent: MeCN, $[NaClO_4] = 0.1$ M. [g] $k_{app} = k_{obsd}/[PHOH]$, standard deviation in runs 1–4, 5–14: $s = 0.648 \times 10^2$, $k_{app} = (5.12 \pm 0.12) \times 10^2$ using 90% confidence limit.

Table II. Pseudo-Second-Order Reaction between $TH\cdot^{+}$ and PHOH[a]

Run no.	$[TH\cdot^{+}] \times 10^4$	$[TH] \times 10^3$	$[PHOH] \times 10^3$	k_{obsd}, $M^{-1}\,s^{-1}$	k_{app}, $M^{-1}\,s^{-1}$
18	0.61	8.98	2	38.6	22.9
19	1.06	8.49	2	48.5	27.6
20	1.06	8.19	2	61.3	34.0
21	1.14	8.55	2	35.1	20.1
22	1.44	7.47	2	59.5	30.9
23	1.52	7.41	2	52.8	27.2
24	5.54	9.34	2	35.8	21.9
25	1.06	8.61	0.5	13.2	30.4
26	1.06	8.98	1	20.0	23.8
27	1.52	7.47	1	29.5	30.6
28	1.21	14	2	34.9	29.5
29	1.37	20	2	22	25.2
30	1.21	23.4	2	18.5	24.3
31	1.29	28.6	2	17.9	28.2
32	0.95	3.61	5	198	25.8
33	1.14	9.04	5	162	38.7
34	1.21	13.7	5	106	35.2
35	1.21	13.7	5	122	40.5
36	1.21	19.5	5	98	43.9
37	1.21	22.7	5	71	36.4
					Av 29.9[b]

[a] Solvent: CH_2Cl_2–TFA (49:1); supporting electrolyte, $n\text{-}Bu_4NBF_4$ (0.1 M); temp 11°C; concentrations in mol/l. $k_{app} = k_{obsd}(2.91 \times 10^{-4} + [TH])/[PHOH]$. [b] Standard deviation: $s = 6.51$, $k_{app} = 29.9 \pm 0.6$ using 90% confidence limit.

At higher $[TH\cdot^{+}]$, the initial complex underwent further oxidation (eq 3) to give the dication complex which lost a proton, accompanied by bond formation (eq 4) to give the sulfonium salt. The latter work invalidated earlier[2] conclusions that the mechanism of the anisylation reaction involved the disproportionation mechanism (eq 5 and 6).

$$2TH\cdot^{+} \rightleftarrows TH^{2+} + TH \qquad (5)$$

$$TH^{2+} + AN \rightarrow (TH\text{-}AN)^{+} + H^{+} \qquad (6)$$

Other electron-transfer reactions of aromatic cation radicals have recently been shown to occur by a mechanism similar to eq 1-4.[1c] Thus, some consistency began to emerge in the mechanism of cation radical reactions. However, the picture again becomes clouded by the recent study of the reactions of $TH\cdot^{+}$ with various benzene derivatives.[3] Kinetic data were reported for reactions of $TH\cdot^{+}$ with phenol (PHOH), acetanilide, and AN in acetonitrile. All the reactions were reported to be second order in the cation radical, and it was noted that AN reacted unusually slow in comparison to the other two substrates. No mechanistic conclusions were arrived at,[3] and it was stated that the low value of the disproportionation equilibrium constant $(\sim 10^{-9})^4$ for $TH\cdot^{+}$ makes the disproportionation mechanism difficult to accept, but no satisfactory alternative mechanism has been proposed which fits the kinetic data. It was also suggested that the reaction with anisole might follow an altogether different mechanism from that of the other two substrates. The latter study[3] gave results which are completely inconsistent with our own study of the kinetics of the reaction of $TH\cdot^{+}$ with phenol. We found that, in either dichloromethane or acetonitrile, the reaction is not second order in $TH\cdot^{+}$ unless there is acid present. Furthermore, the reaction was found to fit the general mechanism which we have proposed for other cation radical reactions.[1b,c] Here we report the results of a kinetic study of the reaction of $TH\cdot^{+}$ with PHOH.

Results

Preliminary studies on the kinetics of the reaction between $TH\cdot^{+}$ and PHOH in both acetonitrile and dichloromethane showed that the reaction is first order in cation radical. The results were not very reproducible in acetonitrile, and thus dichloromethane was chosen as the solvent for the more detailed studies.[12] The kinetic data are summarized in Tables I (first order) and II (second order). Runs conducted in the absence of TFA were found to give excellent pseudo-first-order rate plots which did not deviate from linearity over several half-lives. The runs conducted in the presence of TFA gave linear pseudo-second-order rate plots when the reactions were carried out in the presence of excess unoxidized TH. Examples of the rate plots are illustrated in Figure 1.

Pseudo-First-Order Reaction (Table I). Very little variation was observed in the pseudo-first-order rate constant derived from runs in which $[TH\cdot^{+}]$ was varied by a factor of 5 (runs 1-6). No effect was observed on the rate constant when [TH] was varied by a factor of 4 (runs 1-9). The observed rate constant (k_{obsd}) was found to be directly proportional to [PHOH] (runs 1-9, 10-12), indicating that the reaction is first order in phenol. The rate of the reaction was found to be unaffected by the presence of the more acidic phenol, 2,4,6-trinitrophenol (runs 13 and 14). The data are consistent with rate law 7 where k is the observed second-order rate constant.

$$-d[TH\cdot^{+}]/dt = k[TH\cdot^{+}][PHOH] \qquad (7)$$

Pseudo-Second-Order Reaction. The pseudo-second-order rate constant was found to be markedly dependent upon [TFA] (Table III, runs 38-42). An eightfold decrease in [TFA] brought about a 3×10^3-fold increase in the rate (runs 39 and 42). That the reaction is first order in phenol was demonstrated by the direct proportionality between k_{obsd} and [PHOH] (runs 18-24, 25-27, 33). The dependence of k_{obsd} upon unoxidized TH was derived at two different [PHOH] (runs 18-24, 28-31 with [PHOH] = 2×10^{-3} M and runs 32-37 with [PHOH] = 5×10^{-3} M). Plots of $1/k_{obsd}$ vs. [TH] for the two sets of experiments gave slightly different intercepts. The line shown in Figure 2 was determined by the least-squares procedure on one set of data. The relationship between k_{obsd} and [TH] led to eq 8 to normalize for changes in [TH] and [PHOH]. The rate

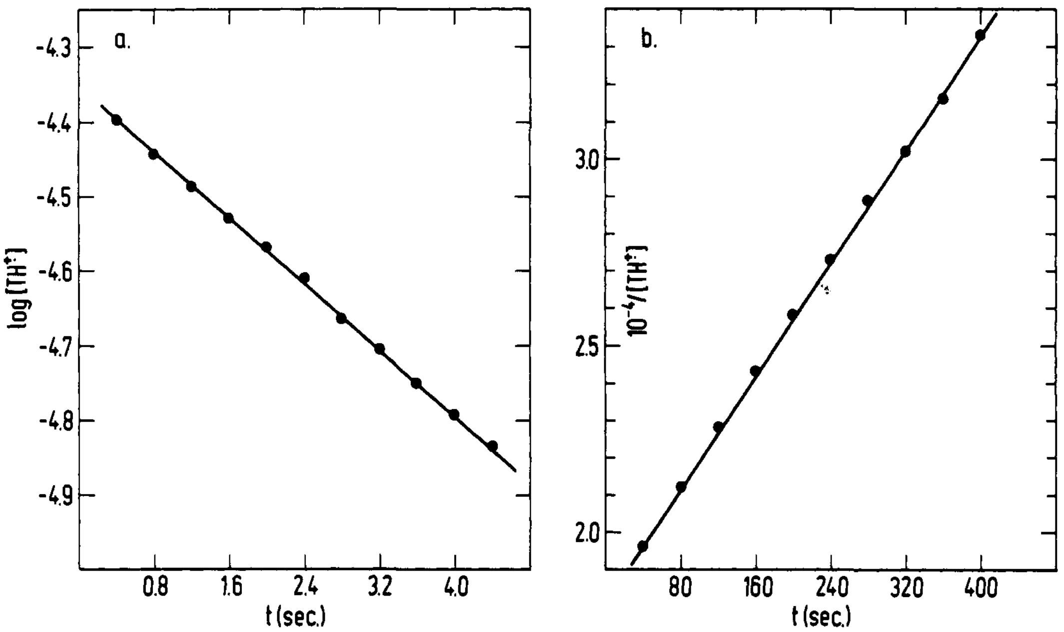


Figure 1. (a) Rate plot for the pseudo-first-order reaction between TH·$^+$ and PHOH in CH_2Cl_2 ($[PHOH]_0 = 5 \times 10^{-4}$ M). (b) Rate plot for the pseudo-second-order reaction between TH·$^+$ and PHOH in CH_2Cl_2:TFA (49:1) ($[TH]_0 = 9 \times 10^{-4}$ M, $[PHOH]_0 = 2 \times 10^{-3}$ M). [n-Bu_4NBF_4] = 0.1 M. Temperature 11°.

Table III. Dependence of $t_{1/2}$ on [TFA] for the Reaction between TH·$^+$ and PHOH in CH_2Cl_2[a]

Run no.	% TFA	$t_{1/2}$, s
38	0	1.4
39	0.5	1.4
40	1	9.8
41	2	441
42	4	4024

[a] Supporting electrolyte, n-Bu_4NBF_4 (0.1 M); temp 11° C. The values for $t_{1/2}$ are calculated at [TH] = 8.5×10^{-4} M, [TH·$^+$] = 10^{-4} M, and [PHOH] = 10^{-3} M.

Table IV. Effect of TFA on the Rate of Anisylation of TH·$^+$[a]

Run no.	[TH·$^+$] × 10^4	[TH] × 10^4	[AN] × 10^2	% TFA	k_{obsd}, $M^{-1}\,s^{-1}$
43	3.57	5.90	9.20	1.0	0.497
44	3.49	6.08	9.20	2.0	0.184
45	3.80	6.02	9.20	4.0	0.061

[a] In dichloromethane containing Bu_4NBF_4 (0.1 M); temp 11.0°C.

law for the pseudo-second-order reaction is given by (9). The constant in the denominator was derived from the mean intercept.

$$k_{obsd} = k_{app}\frac{[PHOH]\ M^{-1}\,s^{-1}}{(2.91 \times 10^{-4} + [TH])} \quad (8)$$

$$-d[TH\cdot^+]/dt = k_{II}[TH\cdot^+]^2[PHOH]/(2.91 \times 10^{-4} + [TH]) \quad (9)$$

Effect of TFA on the Rate of Anisylation of TH·$^+$. The large effect of TFA on the rate of the reaction between TH·$^+$ and PHOH made it necessary to establish whether the effect is solely due to a stabilization of TH·$^+$ or if there is an added specific effect on that particular reaction. The anisylation of TH·$^+$ was chosen due to the obvious similarity between the two reactions. The data are summarized in Table IV. A fourfold increase in [TFA] brought about only an eightfold decrease in the rate constant, only a fraction of the effect observed for the reaction with phenol.

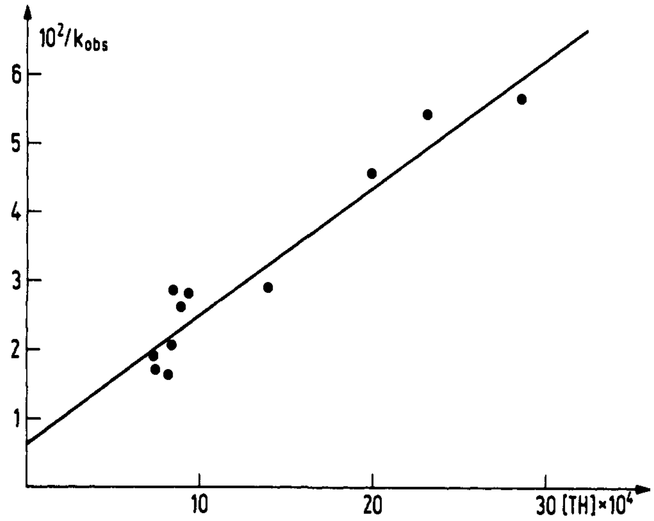


Figure 2. Plot of $1/k_{obsd}$ vs. $[TH]_0$ for the pseudo-second-order reaction between TH·$^+$ and PHOH in CH_2Cl_2:TFA (49:1) at 11°C ($[PHOH]_0 = 2 \times 10^{-3}$ M). The line was obtained after least-squares treatment of the data.

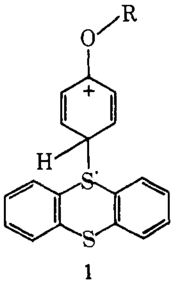
Discussion

Thianthrene cation radical reacts with both anisole and phenol to give thianthrenium salts in which sulfur becomes bonded to carbon para to the methoxy or hydroxy substituent. The kinetics of both reactions are characterized by having both a first and second order in TH·$^+$ segment, the proportions of which are dependent upon the reaction conditions. These similarities suggest that the same mechanisms are probably operative for these similar reactions. However, there is one disturbing feature of this comparison. The pseudo-first-order rate constant for the reaction involving AN[1b] after normalizing for [AN] is equal to about $2.5 \times 10^{-3}\ s^{-1}$, while that involving PHOH is equal to about $5.0 \times 10^2\ s^{-1}$. The corresponding pseudo-second-order rate constants normalized for [nucleophile] and [TH] in CH_2Cl_2 containing 2% TFA are equal to 0.136 for AN[1b] and 29.9 for phenol. Thus PHOH is more reactive than AN by factors of 2×10^5 and 2×10^2 in the first- and second-order reactions, respectively. It is also noteworthy that acetanilide was only about ten times less reactive than phenol when the reaction was conducted in acetonitrile.[3] Thus, it appears that both phenol and acetanilide react with $TH\cdot^+$ abnormally fast compared to anisole when the reactions are conducted under pseudo-first-order conditions. The question then arises as to how phenol and acetanilide differ from AN that would allow them to be so much more reactive than AN in the absence of TFA. If we examine the Hammett relationship discussed by Shine[3] using values for σ^+ of -0.69[5] for *p*-acetamido, -0.77[6] for *p*-methoxy, and -0.92[5] for *p*-hydroxy, we see that a ρ value of about -2.7[3] is obtained for the data for phenol and acetanilide,[3] while a value of about -40 is required for our anisole and phenol data.[13] The latter value is clearly unreasonable for a reaction involving an electrophile attacking an aromatic ring in the rate-determining step of the reaction. However, as will be shown later, the reaction is much more complex than a simple electrophilic substitution, and the Hammett relationship would not necessarily be expected to hold. A structural feature present in both phenol and acetanilide, but absent in anisole, which could possibly account for the large difference in first-order but small difference in pseudo-second-order rate constants, is an ionizable hydrogen. This suggests that the difference in rates might be due to participation of phenolate and acetanilate in the reactions. Thus, for the reaction of phenol, if prior the equilibrium

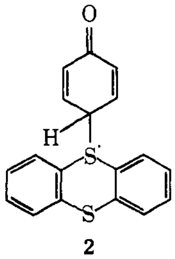
$$\mathrm{PHOH} \rightleftharpoons \mathrm{PHO^-} + \mathrm{H^+} \qquad (10)$$

is involved, we would expect the presence of acid to completely suppress (10) and cause a change in mechanism in going from an acid-free solvent to one containing acid. The pK_a of phenol is 10.0, while that for 2,4,6-trinitrophenol is equal to 0.4.[7] Assuming the same order of acidity in dichloromethane and water leads to the prediction that addition of 2,4,6-trinitrophenol to solutions of phenol should dramatically shift (eq 10) to the left and greatly decrease the rate of any reactions involving PHO^-. The experiments conducted in the presence of 2,4,6-trinitrophenol (runs 9 and 10) do not bear out this prediction; in fact, little change was observed in the rate. Therefore, we can rule out the participation of PHO^- in the reaction of $TH\cdot^+$ with phenol.

The ionizable proton of phenol and acetanilide could give rise to a rate enhancement in still another way. If we consider the first reaction intermediate after the initial encounter complex undergoes bond formation between the positive sulfur atom and the carbon atom para to the substituent (**1**), we see that when R = H (PHOH) proton transfer from oxygen gives the uncharged radical **2**. However, when R = CH_3 (AN), proton transfer from carbon is required to give the uncharged radical **3**. In general, proton transfer from oxygen is fast, while this is not necessarily the case when the proton is being transferred from carbon.[14] Therefore, it is highly probable that the rate differences between the reactions of $TH\cdot^+$ with AN and with the other two substrates arise from the differences in the rates of deprotonation of intermediates such as **1**. The latter suggests that a deuterium kinetic isotope effect should be observed for the phenol reaction. Indeed, k_H/k_D was found to be equal to about 4 (runs 46-48) for the reaction of $TH\cdot^+$ with PHOH.[15]



1



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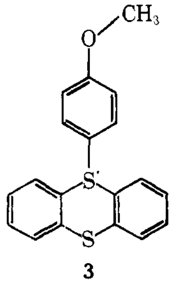


3

Contrary to the previous report,[3] the reaction between PHOH and $TH\cdot^+$ in neutral media, CH_3CN or CH_2Cl_2, follows pseudo-first-order kinetics in $[TH\cdot^+]$. The presence of TFA in either of these solvents had a dramatic effect on not only the rate of the reaction but also on the observed rate law; in the presence of acid, the reaction was observed to be second order in $[TH\cdot^+]$. The reaction of $TH\cdot^+$ with AN has previously been shown to occur by both a first and a second order in cation radical pathway.[1b] Thus, the phenol reaction resembles that with anisole rather closely, with the first order in $[TH\cdot^+]$ reaction being more favorable in the former case. The complexation mechanism[1b] can be formulated for the phenol reaction as shown below:

$$\mathrm{TH\cdot^+} + \mathrm{PHOH} \rightleftharpoons (\mathrm{TH/PHOH})\cdot^+ \qquad (11)$$

$$(\mathrm{TH/PHOH})\cdot^+ \rightleftharpoons (\mathrm{TH\text{-}PHO})\cdot + \mathrm{H^+} \qquad (12)$$

$$(\mathrm{TH\text{-}PHO})\cdot + \mathrm{TH\cdot^+} \rightleftharpoons (\mathrm{TH\text{-}PHO})^+ + \mathrm{TH} \qquad (13)$$

$$(\mathrm{TH/PHOH})\cdot^+ + \mathrm{TH\cdot^+} \rightleftharpoons (\mathrm{TH/PHOH})^{2+} + \mathrm{TH} \qquad (14)$$

$$(\mathrm{TH/PHOH})^{2+} \rightarrow (\mathrm{TH\text{-}PHO})^+ + \mathrm{H^+} \qquad (15)$$

Applying the steady-state approximation to $(\mathrm{TH/PHOH})\cdot^+$, assuming (12) is irreversible under pseudo-first-order conditions, leads to the rate law

$$-\mathrm{d}[\mathrm{TH\cdot^+}]/\mathrm{d}t = \frac{k_{13}k_{12}[\mathrm{TH\cdot^+}][\mathrm{PHOH}]}{(k_{-12} + k_{13})} \qquad (16)$$

which has the form of the observed rate law 7. This rate law is also consistent with the observed kinetic isotope effect. The influence of TFA upon the rate and the reaction pathway is connected to (12). Thus, the presence of acid slows the deprotonation while it has no effect upon (14) which predominates resulting in the observation of pseudo-second-order kinetics.

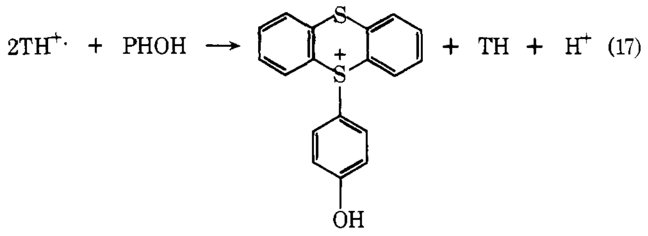
As implied above, either of the two different reaction pathways (11,12,13 or 11,14,15) can predominate depending upon the reaction conditions. In neutral solvents, reaction 12 is fast and completely precludes the occurrence of the second-order reaction 14, and thus only 11,12,13 is observed. When the solvent is made acidic, reaction 12 is inhibited, and further electron transfer (eq 14) predominates, and (11,14,15) is the exclusive reaction pathway. Since (12) is a first-order step and (14) second-order, it might be possible to change the relative importance of the two reactions by drastically changing $[TH\cdot^+]$. However, no change in mechanism was observed over the concentration range of $TH\cdot^+$ investigated. Such a mechanism change was observed in the previous study.[1b]

The dependence of k_{obsd} on $[PHOH]_0$ shows that the reaction is clearly first order in phenol. As in the case of the anisylation reaction,[1b] the disproportionation mechanism[3] predicts a less than first-order dependence on [PHOH]. Thus, both the observation of pseudo-first-order kinetics and the first-order phenol dependence clearly eliminates the disproportionation mechanism from further consideration.

Experimental Section

Acetonitrile and dichloromethane were reagent grade and passed through a column of neutral alumina (Woelm W 200) immediately before use. Trifluoroacetic acid and trifluoroacetic acid anhydride were Fluka (purum grade) and used as obtained.

The apparatus used for voltametric measurements has been described.[9] The cell used both for the kinetic study and for the preparation of the thianthrene cation radical solutions was a cylindrical, round-bottom, jacketed container with openings for the auxiliary electrode compartment, reference electrode, inert gas supply, thermometer, and a Beckman rotating disk electrode. The temperature was controlled with tap water. The thianthrene cation radical solutions were prepared by partial oxidation of solutions of the compound in the solvent systems. Oxidations were carried out at constant current (25.0 mA) at a large area platinum gauze electrode. Current was passed for a time calculated to give the desired concentration of cation radical. The concentration of cation radical was determined exactly after oxidation by the magnitude of the limiting current at the rotating disk electrode. The limiting current was followed as a function of time for several minutes, and little or no decrease in cation radical concentration was observed before adding the phenol solution. The procedure used for carrying out the kinetic runs was that previously described.[10] $TH\cdot^{+}ClO_4$ (1.0 mmol), prepared according to a literature procedure,[11] was allowed to react with PHOH (1.0 mmol) in three solvents: acetonitrile, dichloromethane, and dichloromethane-TFA (49:1). The product, isolated as before,[3] was the same in all three cases and was identified as 5-(*p*-hydroxyphenyl)thianthrenium (**4**) perchlorate by its ultraviolet absorption spectrum.[3] The stoichiometry of the reaction was previously[3] shown to follow (17).



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References and Notes

(1) For other parts in the series, see (a) U. Svanholm, A. Ronlán, and V. D. Parker, *J. Am. Chem. Soc.*, **96**, 5108 (1974); (b) U. Svanholm, O. Hammerich, and V. D. Parker, *ibid.*, **97**, 101 (1975); (c) U. Svanholm and V. D. Parker, *ibid.*, submitted for publication.
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(12) Very poor reproducibility was reported for the reactions of $TH\cdot^{+}$ with AN and acetanilide.[3] For example, the rate constants reported for acetanilide varied by a factor of about 5 and those for AN by a factor of about 6. At least some of this variation must be attributed to difficult to control background reactions.
(13) The value calculated by Shine[3] for their data was −16.7.
(14) Proton transfer reactions are discussed in detail in ref 8.
(15) Rate constants for the reaction of $TH\cdot^{+}$ with PHOD were difficult to reproduce This of course was due to the low PHOD concentrations used (5×10^{-4} M). The presence of trace amounts of water, which we were unable to avoid even though scrupulously dry solvent was used, markedly affects the PHOD/PHOH ratio and hence tends to diminish the apparent kinetic isotope effect. The isotope effect observed, $k_H/k_D = 2$, is much lower than the real value. After one run, the reaction mixture was evaporated under argon and the NMR spectrum showed that the isotopic purity was less than 50%.

Internal Heavy-Atom Effects on the Photodimerization of Acenaphthylene[1]

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Abstract: The quantum yields of dimerization of 5,6-dichloroacenaphthylene were measured at 365 nm as a function of ethyl iodide concentration, substrate concentration, and quencher concentration. The product distributions in each case were also determined. Except for the relative triplet efficiencies, the photochemistry of this compound appears to be analogous to that of acenaphthylene. The results of this study indicate that internal heavy atoms have a considerable influence on both $T_1 \leftarrow S_1$ and $S_0 \leftarrow T_1$, unlike the external heavy-atom case in which the former process was far more sensitive to heavy-atom perturbation. A mechanism consistent with the data is proposed, and the triplet rate constants for dimerization and the various decay modes have been determined.

External heavy-atom effects on the dimerization and cycloaddition reactions of acenaphthylene have been the subject of a number of recent studies.[2] Solvents containing either bromine or iodine have been shown to produce a dramatic increase in the steady-state triplet population of acenaphthylene by increasing the rate of intersystem crossing, $T_1 \leftarrow S_1$.[3] As a result, numerous changes in the photochemistry of acenaphthylene in the presence of heavy-atom solvents have been observed.[4]

We recently reported a detailed mechanistic study on the effect of ethyl iodide on the photochemistry of acenaphthylene.[2g,h] As an extension of our studies on photochemical heavy-atom effects, we have now investigated the photochemistry of 5,6-dichloroacenaphthylene in order to compare internal and external heavy-atom perturbation.[5]

Results

(A) **Photoproducts.** The two major photoproducts resulting from the irradiation of 5,6-dichloroacenaphthylene have been identified as the cis cyclobutane dimer and the trans cyclobutane dimer, as illustrated in Chart I. Some difficulties were initially encountered in the separation, purification, and identification of these products as a result of both the relatively high-melting points of these dimers and their low solubilities in all organic solvents used, precluding the use of such analytical techniques as NMR, GLC, high-pressure liquid chromatography, and mass spectral analysis. By utilizing the knowledge of the photochemistry of acenaphthylene gained in previous studies, however, these difficulties were circumvented.