Although the values under method 1 do not pose serious problems, the ξ_C^2 value obtained by method 2 is quite small and is nearly half that of ξ_H^2. This anomaly should be due to the still remaining errors in the intensity ratios. In order to visualize this let us arbitrarily vary the intensities, very slightly, to fit the experimental ratio to the theoretical ratio. These approximated intensities along with their ratios and resultant ξ_α^2 values are given in Table IV under step 2. All ξ_α^2 values now are fairly satisfactory except for slightly lower value of ξ_C^2 in method 2, which is mainly due to the 1.68% error involved in the ratio of ω_5 (Table II). The correction added in the above step to τ_3 is only 0.005 m^2/mol which falls within the experimental uncertainities. The correction to τ_5 is 0.074 m^2/mol and is well beyond the experimental uncertainities. Hence the inequality of all four ξ_α^2 values given in Table IV is because the experimental isotopic intensity ratios are not found to be satisfactory.

This statistical picture would not have been so clear if we had used the fact that $\xi_C = \xi_H$ in method 2 (or eq 9) because essentially we will end up with the same values as those obtained in method 1. Perhaps this advantage may reflect the greater impact of eq 9 in reducing the infrared band intensities when used in conjunction with eq 8 for finding the errors in the ratios of isotopic intensities. Though the errors realized above are not very large, they have been magnified when eq 8 and 9 are used simultaneously which enabled us to obtain a reasonable quantitative picture.

Acknowledgment. The author is thankful to Dr. Surjit Singh for many helpful discussions and to CSIR, India for an award of a post doctoral fellowship.

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Studies of Sulfonyl Radicals. 4. Flash Photolysis of Aromatic Sulfones

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(Received May 25, 1977)

Publication costs assisted by the Chemical Research Institut of Non-Aqueous Solutions

The flash photolysis of arenesulfonyl iodides and some other aromatic sulfones showed a transient absorption spectrum with a maximum near 330 nm and a continuous band up to 500 nm which was attributed to the arenesulfonyl radical. No wavelength shift in the absorption maximum was observed for substituted benzenesulfonyl radicals. The second-order decay rates of the radicals are shown to be diffusion controlled and the rate constants are about 5 × 10^8 M^{-1} s^{-1}.

Introduction

Sulfonyl radicals are considered as important intermediates in many processes in organic chemistry. They are well accepted as intermediates in the radical copolymerization of SO_2 with various vinyl monomers to form polysulfones,[1-3] and in the thermal and photochemical decomposition of sulfonyl halides,[4,5] diarylsulfones,[6] diaryldisulfones,[7] and azosulfones.[8] Recently, some research papers[9] have dealt with their reactivities since they are concerned with the mechanism of SO_2 removal from polluted air. Although a number of electron spin resonance studies on alkane and arenesulfonyl radicals have been reported,[10,11] there are few papers in the literature dealing with the optical absorption of these radicals. Bjellqvist and Reitberger[12] reported an absorption maximum at 355 nm for the cyclohexanesulfonyl radical. Eriksen and Lind[13] found an absorption maximum at 332 nm for alkanesulfonyl radicals formed by pulse radiolysis of alkanesulfonyl chlorides. In both of the studies the decay rate constants have not been determined. In a continuation of our studies[14] on the reactivities of sulfonyl radicals, we report here the absorption spectra and decay rate constants of the arenesulfonyl radicals produced by the flash photolysis of some aromatic sulfones.

Experimental Section

A conventional flash photolysis apparatus, as described by Porter and West,[15] was used for the present work. A photoflash lamp of 100 J with a half-duration of about 20 μs was used.

All experiments were performed at 23 ± 2 °C. The data were derived from the first flash delivered to a fresh solution.

All the solvents used were of spectroscopic grade. They were distilled under vacuum before use.

Arenesulfinic acids and their salts were prepared from the corresponding arenesulfonyl chlorides following the procedure described in the literature.[16] They were recrystallized twice from water. Arenesulfonyl iodides were prepared from their corresponding sodium arenesulfinates.[17] These compounds were recrystallized twice from carbon tetrachloride, dried under reduced pressure at low temperature (about at −20 °C), and stored in a refrigerator at −20 °C.[14] 2,4,6-Triisopropylbenzenesulfonyl iodide is

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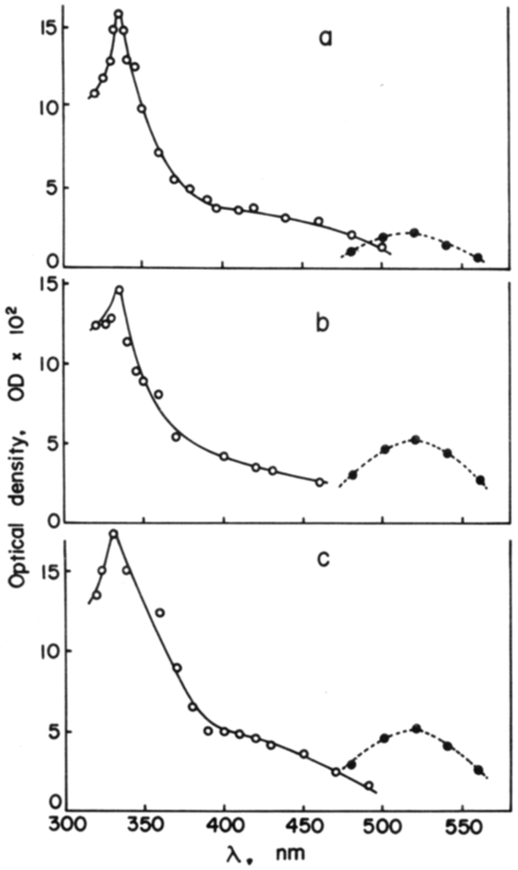

Figure 1. Absorption spectra produced by the flash photolysis of arenesulfonyl iodides in degassed CCl_4: [arenesulfonyl iodide] = 10^{-4} M, 290-nm filter cutoff was used: (○) OD_{75}–OD_∞; (●) OD_∞, where OD_{75} and OD_∞ represent the optical density read 75 and 1000 μs after the flash, respectively; (a) *p*-toluenesulfonyl iodide, (b) benzenesulfonyl iodide, (c) *p*-chlorobenzenesulfonyl iodide.

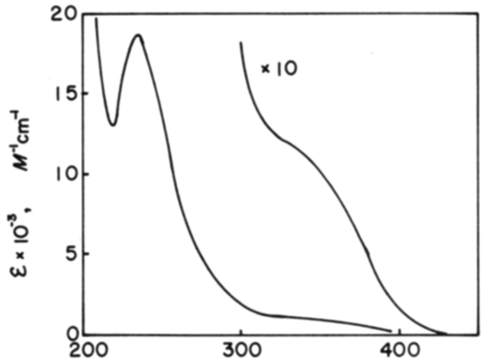

Figure 2. Absorption spectra of *p*-toluenesulfonyl iodide in CCl_4.

not as stable, it was used soon after recrystallization. (Calcd for $C_{15}H_{23}ISO_2$: C, 45.69; H, 5.87 Found: C, 45.45; H, 5.51.) Diphenyl disulfone was synthesized according to the method of Denzer et al.[18]

Results and Discussion

1. *Absorption Spectra of the Transient Species Produced by the Flash Photolysis of Arenesulfonyl Iodides.* Flash photolysis of arenesulfonyl iodides in CCl_4 resulted in a transient absorption with a maximum near 330 nm and a continuous band up to 500 nm, as shown in Figure 1. A typical absorption spectrum of the starting material, *p*-toluenesulfonyl iodide, is shown in Figure 2. Three typical oscilloscope traces showing the decay of the transient species are shown in Figure 3. In the region where arenesulfonyl iodides exhibit absorption, the oscilloscope trace in Figure 3a indicates that some arenesulfonyl iodides have reacted. In the 450–550-nm region the results in Figure 3c show the formation of a permanent product. This permanent product which has an absorption with maximum at 520 nm in CCl_4, as shown in Figure 1, is attributed to I_2. In the region where the absorption of both the starting material and I_2 product is negligible, the observed decay of the transient is shown in Figure 3b. The photolysis of arenesulfonyl iodides was reported[4,19] to be a homolytic sulfur–iodine bond cleavage process leading to the formation of sulfonyl radical and iodine radical. On the basis of the above considerations, the three most probable assignments for the transient spectra would be the arenesulfonyl radical, the I atom–solvent charge transfer band, and the triplet state of arenesulfonyl iodide.

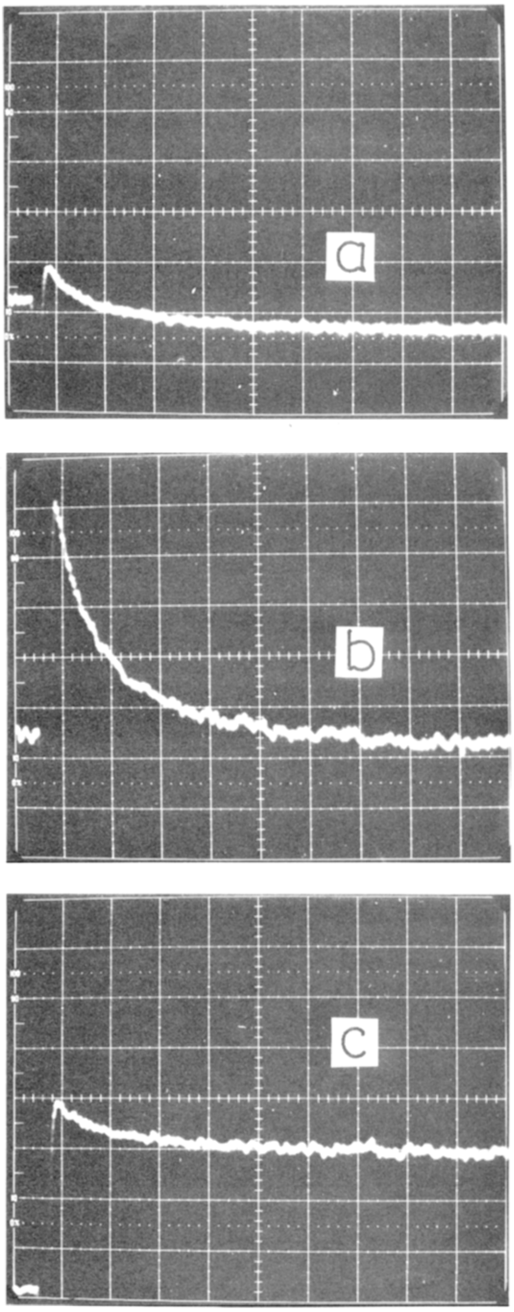

Figure 3. Oscillograms showing the transient decay in transmittancy at (a) 320 nm, (b) 420 nm, (c) 520 nm, following flash photolysis of *p*-toluenesulfonyl iodide in CCl_4. Sweep time equals 200 μs per major division; vertical scale corresponds to a decrease in transmittance equal to 20% per major division for (a) and 2% for (b) and (c).

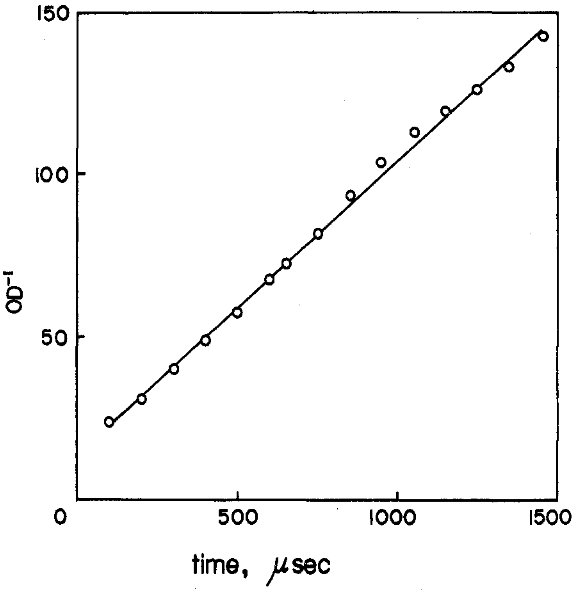

Figure 4. Second-order plot of the decay at 420 nm of the presumed *p*-toluenesulfonyl radical formed by the flash photolysis of *p*-toluenesulfonyl iodide in liquid paraffin.

TABLE I: Dependence of the Decay Rate of the Presumed *p*-Toluenesulfonyl Radical[a] on the Solvent Viscosity

Solvent	η,[b] cP (at 20 °C)	$1/\eta$	$k/\epsilon \times 10^{-4}$,[c] cm s^{-1}
n-Hexane	0.320	3.125	70 ± 9.2[d]
CCl_4	0.965	1.036	27 ± 2.3
Cyclohexane	0.980	1.020	36 ± 3.8
Paraffin	21.76	0.046	8.8 ± 1.4

[a] The radical produced by the flash photolysis of *p*-toluenesulfonyl iodide in degassed solvents. [b] "Technique of Organic Chemistry", Vol. 2, 3rd ed, J. A. Riddick and W. B. Bunger, Ed., Wiley-Interscience, New York, N.Y., 1970. [c] Values obtained from the second-order plot of the transient decay at 420 nm. [d] Standard deviation.

Although the I atom gives a charge transfer band with various solvents such as aromatic hydrocarbons,[20] alcohols,[21] and liquid alkanes,[22] it was found[22] that the $I-CCl_4$ charge transfer band is below 310 nm. Furthermore, the possible triplet band of arenesulfonyl iodide may be excluded on the basis of the following considerations: (a) The absorbance of arenesulfonyl iodide decreased after the flash and I_2 was formed. The amount of arenesulfonyl iodide reacted is equal to the half of the amount of I_2 formed. (b) The transient was also observed even in the aerated solution. Therefore, the transient absorption spectra observed in the flash photolysis of arenesulfonyl iodide are attributed to arenesulfonyl radicals.

Absorption of arenesulfonyl iodide prevented an accurate measurement of λ_{max} of the absorption spectra of the transients. However, within experimental error, the effects of the substituents on the aromatic ring of arenesulfonyl radicals on λ_{max} were not observed.

2. *Effects of Solvent Viscosity on the Decay Rate Constants.* The second-order decay rate constant of sulfonyl radicals, k, is defined by the equation

$$-d[ArSO_2\cdot]/dt = k[ArSO_2\cdot]^2 \qquad k = \epsilon l d(1/OD)/dt$$

where ϵ is the extinction coefficient for the arenesulfonyl radical, l is the optical path length of the analytical flash, and OD is the optical density of the sulfonyl radical. A typical second-order plot for the decay of arenesulfonyl radicals is shown in Figure 4. The plot shows that the decay of the *p*-toluenesulfonyl radical follows second-order kinetics up to 80% conversion. The slope of the plot yields the ratio k/ϵ. The results in Table I show that the k/ϵ value increased with decreasing viscosity of solvents. As can be observed from the plot in Figure 5, a fairly good linear correlation was obtained. These results show that the bimolecular reaction of sulfonyl radicals is diffusion controlled.

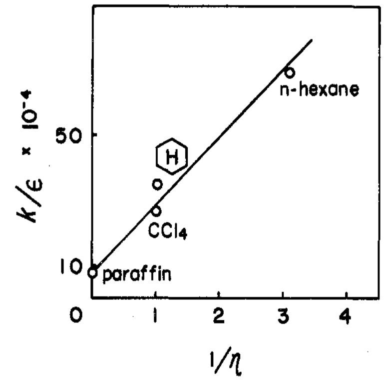

Figure 5. Plot of k/ϵ against $1/\eta$ for *p*-toluenesulfonyl radical in various solvents (see Table I).

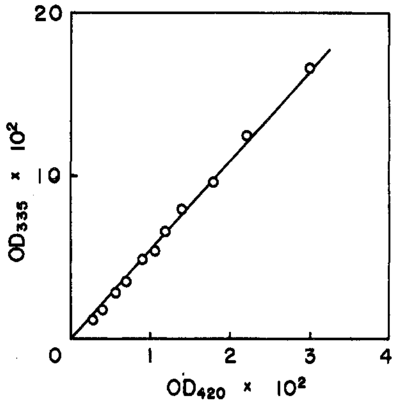

Figure 6. Plot of ($OD_t - OD_\infty$) at 335 nm vs. ($OD_t - OD_\infty$) at 420 nm for the transient species produced by the flash photolysis of *p*-toluenesulfonyl iodide in CCl_4, where OD_t and OD_∞ represent the optical density read 75 and 1000 μs after the flash, respectively.

3. *Estimation of ϵ and K.* The photolysis processes for arenesulfonyl iodides are logically proposed as

$$ArSO_2I \xrightarrow{h\nu} ArSO_2\cdot + I \qquad (1)$$

$$ArSO_2\cdot + I \rightarrow ArSO_2I \qquad (2)$$

$$2I \xrightarrow{k_{I_2}} I_2 \qquad (3)$$

$$2ArSO_2\cdot \xrightarrow{k_t} \text{products}^4 \qquad (4)$$

Based on the concentration of I_2 formed and assuming that process 2 is of little importance compared with the other processes, we can estimate the initial concentration of arenesulfonyl radicals formed and then ϵ and k. The above assumption is reasonable for the following reasons: (a) The plot of the optical density at 335 nm vs. that at 420 nm of sulfonyl radicals at various times is a straight line and passes through the origin, as shown in Figure 6. If process 2 is important the re-formation of *p*-toluenesulfonyl iodide should affect the decay of the radical at 335 nm while it gives no effect on the decay kinetics at 420 nm. Consequently, the plot would not pass through the origin. It is noted that the molar extinction coefficients for *p*-toluenesulfonyl iodide in CCl_4 at 335 and 420 nm are 1200 and 50, respectively. (b) The estimated k_t is about 10^8 M^{-1} s^{-1}, then we have $k_t \ll k_{I_2}$, since the value of k_{I_2}

TABLE II: Decay Kinetics of the Presumed Arenesulfonyl Radicals in Degassed CCl_4

System	Decay, $k \times 10^{-8}$,[a] $M^{-1}\ s^{-1}$ (at 23 °C)
p-Toluenesulfonyl iodide	5.0 ± 1.5[b]
Benzenesulfonyl iodide	3.4 ± 1.3
p-Chlorobenzenesulfonyl iodide	4.7 ± 1.3
2,4,6-Triisopropylbenzenesulfonyl iodide	0.8 ± 0.2

[a] Second-order decay kinetics were measured at 420 nm, except for 2,4,6-triisopropylbenzenesulfonyl iodide whose *k* was measured at 440 nm. [b] Standard deviation.

TABLE III: Absorption Maxima and Decay Rate Constants of Some Radicals

Radical	λ_{max}, nm	$k \times 10^{-9}$,[a] $M^{-1}\ s^{-1}$	$k_D \times 10^{-9}$,[b] $M^{-1}\ s^{-1}$	Solvent
$C_6H_5CH_2\cdot$	318,[c] 453	0.68[d]	12.2	CH_3OH
$CH_3\cdot$	216[e]			Gas phase
$C_6H_5NH\cdot$	308,[c] 400	1.5[f]	6.6	H_2O
$C_6H_5O\cdot$	300,[c] 402	0.79[g]	6.6	H_2O
$C_6H_5S\cdot$	297,[h] ~500	2.8[h]	20	*n*-Hexane
$RS\cdot$	330[i]			H_2O
$ArSO_2\cdot$	335[j]	0.37–0.5[j]	6.7	CCl_4
$RSO_2\cdot$	332[k]			H_2O

[a] At 25 ± 3 °C. [b] Diffusion-controlled rate constant calculated using the Debye equation, $k_D = 8RT/3000\eta$ $M^{-1}\ s^{-1}$. [c] Reference 24. [d] Reference 25. [e] Reference 26. [f] Reference 27. [g] Reference 28. [h] Reference 29. [i] Reference 30, R = $H_3^+NCH_2CH_2S$–, $HOOCCH_2CH_2$–. [j] This work. [k] Reference 13, R = CH_3–, C_2H_5–, and C_3H_7–.

was reported to be $19 \times 10^9\ M^{-1}\ s^{-1}$.[23] This means that almost all I atoms will be consumed by self-recombination reaction 3.

By extrapolating the second-order plot (Figure 4) to zero time, we can obtain the value of the initial optical density of sulfonyl radicals; if the initial concentration of sulfonyl radicals is known the extinction coefficient can therefore be calculated. We can calculate the initial concentration of sulfonyl radicals from the concentration of I_2 formed in a given flash which is calculated from the difference between the absorbances of the reaction mixture before and after the flash from the oscilloscope trace in Figure 3c. Similarly, the initial concentration of sulfonyl radical can also be calculated based on the concentration of arenesulfonyl iodide consumed in a given flash from the oscilloscope trace in Figure 3a. The two procedures yield similar value of the initial concentration of sulfonyl radical within experimental error. However, we use the former procedure, calculation based on the concentration of I_2 formed, in order to estimate the value of the decay rate constants, since this procedure is more accurate. For example, the estimated values of initial concentration of *p*-toluenesulfonyl radical formed in a given flash, based on the disappearance of *p*-toluenesulfonyl iodide and on the amount of I_2 formed, are $5 \pm 2 \times 10^{-6}$ and $6 \pm 1 \times 10^{-6}$ M, in the photolysis of 1×10^{-4} M *p*-toluenesulfonyl iodide in degassed CCl_4, respectively.

Second-order decay rate constants for benzene-, *p*-toluene-, and *p*-chlorobenzenesulfonyl radicals are practically equal, as shown in Table II. However, the 2,4,6-triisopropylbenzenesulfonyl radical, being a sterically hindered radical, has a decay rate constant somewhat smaller.

4. *Properties of Arenesulfonyl Radicals.* For comparison purposes the data on the absorption maxima and decay rate constants of some isoelectronic radicals reported by other workers are listed in Table III together with our results on sulfonyl radicals. The absorption spectra of the isoelectronic radicals such as benzyl, anilino, phenoxyl, and thiophenoxyl radicals consist of two distinct systems, a sharp band near 300 nm and another transition in the 400–500-nm region. Both the ~300- and ~400-nm bands were assigned[24] as π–π^* transition. In these π type radicals, for example, the benzyl radical, the unpaired electron is delocalized into the phenyl ring so that its absorption maxima are quite different from that of the methyl radical. Similarly, the absorption bands of the thiophenoxyl radical are distinct from that of alkanethiyl radicals (see Table III). The spectra of arenesulfonyl radical display a continuous band up to 500 nm, however, apart from the above-mentioned isoelectronic radicals, there is no observable maximum in the 400–500-nm region. Furthermore, the absorption maximum of the arenesulfonyl radical is very near to that of the alkanesulfonyl radical. From this viewpoint, we believe that the 335-nm band of the sulfonyl radical is due to the transition of the unpaired electron within the SO_2 moiety. Namely, the arenesulfonyl radical has σ character with respect to the phenyl ring. This assignment is supported by ESR studies of the sulfonyl radical[11] in which it has been shown that the unpaired electron is localized mainly on the SO_2 moiety and that sulfonyl radical is a σ-like radical. Molecular orbital (MO) calculations on the electronic spectra of the sulfonyl radical would give an opportunity to judge properly this assignment, unfortunately, there are, till now, no available data on MO calculations for sulfonyl radicals.

Our values obtained for the decay rate constants for arenesulfonyl radicals (Table II), with the exception of the hindered 2,4,6-triisopropylbenzenesulfonyl radical, are near the diffusion-controlled limit, and are insensitive to substituents. This is in agreement with the results in section 2 in which we have shown that the bimolecular reaction of the sulfonyl radical is diffusion controlled. If we take solvent viscosity into consideration, the measured values of the decay rate constants in Table III are comparable. All experimental decay rate constants are smaller than the calculated diffusion-controlled rate constants. This may be attributed to the small activation energy of recombination.

5. *Transient Absorption Spectra Produced by Flash Photolysis of Other Aromatic Sulfones. Arenesulfonyl Acids and Their Sodium Salts.* The flash photolysis of aqueous solutions of sodium arenesulfinates gives a transient absorption with a maximum near 315 nm and a continuous band up to 500 nm, as shown in Figure 7a. It is expected that the sulfonyl radical is formed by the photoejection of an electron from the arenesulfinate anion. However, no transient absorption at 700 nm due to the hydrated electron could be observed. A possible explanation is that the hydrated electron has been formed but it decayed during the flash duration due to its high reactivity. The transient spectrum observed from arenesulfinic acids is identical with that of their sodium salts. No wavelength shift was observed in the λ_{max} of the transient spectrum produced by the flash photolysis of benzene-, *p*-toluene-, *p*-chlorobenzenesulfinic acids and their sodium salts.

Diphenyl Sulfone. The flash photolysis of diphenyl sulfone in degassed acetonitrile produced a transient absorption with a maximum near 330 nm (Figure 7b). In the steady state photolysis of diphenyl sulfone, it has been suggested that the C–S bond is cleaved on photolysis leading to the formation of the sulfonyl and phenyl radical.[31]

Diphenyl Disulfone. The formation of the benzenesulfonyl radical in the photolysis of diphenyl disulfone by

TABLE IV: Absorption Maxima and Decay Kinetics of Radicals Produced in the Flash Photolysis of Some Aromatic Sulfones

System[a]	Solvent	η, cP (at 20 °C)	λ_{max}, nm	Decay, $k/\epsilon \times 10^{-4}$,[b] cm s^{-1} (at 320 nm)
p-Toluenesulfonyl iodide	CCl_4	0.965	335	6.8 ± 1.0[d]
Benzenesulfonyl iodide	CCl_4	0.965	335	5.1 ± 1.0
p-Toluenesulfinic acid	Cyclohexane	0.980	315	9.8 ± 2.1[c]
Sodium p-toluenesulfinate	H_2O	1.002	315	5.5 ± 1.2
Diphenyl sulfone	CH_3CN	0.350	330	17.3 ± 2.3
Diphenyl disulfone	CH_3CN	0.350	320	18.4 ± 2.4

[a] In degassed solution. [b] Calculated from the slope of the initial part (about 70% conversion) of the plot of $1/(OD_t - OD_\infty)$ vs. time, where OD_t and OD_∞ represent the optical density of the transient at time t and that of permanent product, respectively. [c] Measured at 315 nm. [d] Standard deviation.

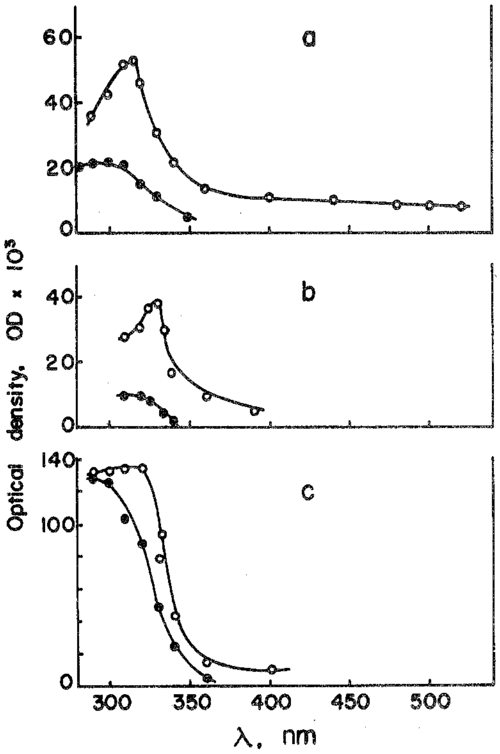

Figure 7. Absorption spectra observed from the flash photolysis of (a) aqueous solution of sodium p-toluenesulfinate, (b) diphenyl sulfone, and (c) diphenyl disulfone in degassed acetonitrile. Optical density read 100 (○) and at 1000 μs (●) after the flash. A 250-nm cutoff filter was used.

a S–S bond scission was proposed.[7] The absorption spectra observed in the flash photolysis of diphenyl disulfone is shown in Figure 7c.

All the aromatic sulfones showed a permanent absorption with a maximum near 300 nm. This absorption was much stronger in the case of diphenyl disulfone. The final products isolated from the termination of sulfonyl radicals such as diphenyl disulfone (1), sulfonic anhydride (3), and thiosulfonate (4),[4] are not likely responsible for this permanent absorption since they do not display an absorption maximum at 300 nm. A possible candidate for this permanent product may be sulfonic–sulfinic anhydride (2).[4] However, better information about lifetime and absorption spectra on this unstable compound is necessary to evaluate it properly.

As shown in Table IV, λ_{max} for the transient species obtained from diphenyl sulfone and diphenyl disulfone are practically identical with those obtained from arenesulfonyl iodides. The λ_{max} of the transient species obtained from arenesulfinic acids and their sodium salts shifted toward the shorter wavelength side. A straightforward explanation for the shift is not known. The slope (k/ϵ) of the $1/(OD_t - OD_\infty)$ vs. time was estimated. A typical second-order decay of the transient species is shown in Figure 8. The value of k/ϵ was measured in different solvents due to the problem of solubility of these sulfones, however, if the viscosity of solvent is taken into consideration, the value of k/ϵ for all the transient species at the wavelength are practically equal. From this viewpoint, we may expect that the transient species produced in the flash photolysis of the aromatic sulfones are identical, i.e., they are the sulfonyl radicals.

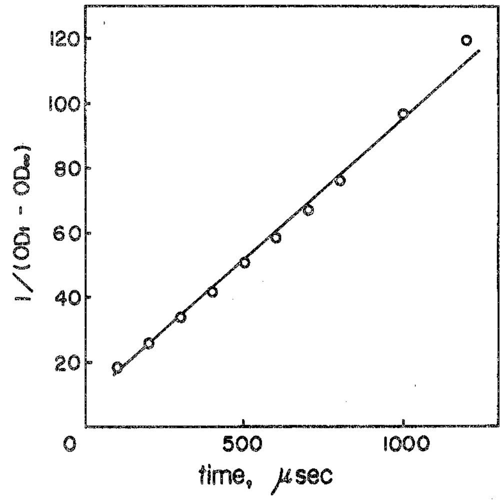

Figure 8. Decay at 315 nm of the transient species formed by the flash photolysis of p-toluenesulfinic acid in cyclohexane. OD_t and OD_∞ represent the optical density at time t and 4 ms after flash, respectively.

Conclusions

1. The transient species obtained in the flash photolysis of the above-mentioned aromatic sulfones are the corresponding arenesulfonyl radicals, since the absorption is common to the photolysis of different molecules.
2. The decay rate for arenesulfonyl radicals was found to be diffusion controlled.
3. No wavelength shift in the absorption maximum was observed for substituted benzenesulfonyl radical. It is concluded that the unpaired electron of the sulfonyl radical is localized mainly on the SO_2 moiety.

Acknowledgment. The present work was supported by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education (047018, 1976). One of the authors (H. H. Thoi) expresses his thanks to the Japanese Ministry of Education for the award of a scholarship during this investigation.

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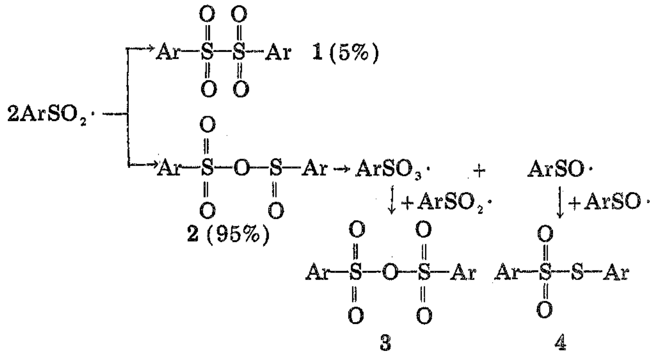

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Carbon-13 Chemical Shifts of Gaseous Four-Carbon Hydrocarbons. Comparison of Shifts in the Liquid, Gaseous, and Adsorbed States

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Publication costs assisted by the National Research Council of Canada

The ^{13}C chemical shifts of the gaseous butanes, butenes, butynes, and 1,3-butadiene have been measured. All of these molecules experience a downfield shift on going from gas to liquid. This shift is greater for the peripheral carbons of each molecule. The same molecules have been studied adsorbed on hydroxylated SiO_2. The shift from gas to adsorbed state is small for aliphatic carbons but larger than the gas–liquid shift for multiple-bonded carbons.

Introduction

The ^{13}C chemical shifts of butenes on various adsorbents have recently been measured.[1-4] While these data potentially contain valuable information about the nature of the interaction between the adsorbent and adsorbate, their interpretation is not, at present, entirely clear. It is only in the case of Ag$^+$ zeolites as adsorbents[4] that comparison with butene–Ag$^+$ complexes in solution enables a simple conclusion to be drawn: that analogous complexes are formed in the zeolite.

One possible problem of interpretation is the state of the hydrocarbon which is used as a reference. All of the data to date have been referred to the neat liquid hydrocarbon, but for interpretative purposes, one would prefer to have shifts relative to isolated, i.e., gaseous, hydrocarbon molecules. There are few data extant[5] which enable one to say whether a significant shift difference exists between gas and liquid. Such shifts are normally less than 1 ppm for ^{1}H, but can be as large as 10 ppm for ^{19}F.[5] One might reasonably expect intermediate values for ^{13}C, which could easily confuse interpretation of adsorption shifts, which are typically of the order of a few parts per million. The only available ^{13}C measurement appears to be that of Tiffon and Doucet[6] for *n*-pentane, where shifts of up to 2.8 ppm were found.

In order to clarify the situation, we have measured the gas to liquid ^{13}C chemical shift differences for the butanes, butenes, butynes, and 1,3-butadiene. The C_4 hydrocarbons are a favorable case for such measurements, since their vapor pressures, a few atmospheres at ambient temperatures, permit a high enough gas phase concentration, while at the same time not requiring special high pressure apparatus for the study of the neat liquids. In addition to the gas phase measurements, we have carried out studies of the butanes, butynes, and 1,3-butadiene adsorbed on SiO_2, for comparison with our previous studies on the butenes.[1]

Experimental Section

All gases were CP grade from Matheson of Canada Ltd., except for the butynes, which were obtained from Cygni Chemical Corp. The hydrocarbons were purified by

0022-3654/78/2082-0319$01.00/0