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Reaction between *p*-Toluenesulfinic Acid and Diphenyldiazomethane[1)]

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Reaction between *p*-toluenesulfinic acid and diphenyldiazomethane was investigated in several solvents. Reaction was faster in non-polar solvents and slower in polar solvents. Experiments with $CH_3C_6H_4SO_2D$ showed that protonation of diphenyldiazomethane is the rate-determining step. In non-polar solvents the main product was benzhydryl *p*-tolyl sulfone, whereas in polar solvents benzhydryl *p*-toluenesulfinate was the main product. In ethanol, benzhydryl ethyl ether was also produced. The mechanism of the reaction was discussed.

Although the formation of methyl sulfinates from sulfinic acids and diazomethane is known for a long time,[2)] no reactions of sulfinic acids with other aliphatic diazo compounds have been reported. Since sulfinate anions are ambident, alkylation may give rise to sulfinate esters and sulfones. Ordinary alkylating agents yield sulfones alone,[3)] whereas such powerful alkylating agents as triethyloxonium tetrafluoroborate give ethyl sulfinates as the main products.[4)] Relative yields of esters and sulfones are influenced by the solvent.[5)]

The kinetics and products of the reaction between *p*-toluenesulfinic acid and diphenyldiazomethane has been investigated, and the results are given in this paper.

Results and Discussion

Kinetic Studies. The rate of decrease of diphenyldiazomethane (I) was determined by use of the decrease of the absorption of I at 525 nm. The reaction was of first order in both *p*-toluenesulfinic acid (II) and I. Rates of the reaction were considerably different in various solvents; they were quite large in benzene or dichloromethane and much smaller in dioxane, alcohol or dimethyl sulfoxide. The rate constants in various solvents are shown in Table 1. When the logarithms of the rate constants determined at various temperatures were plotted against $1/T$, good straight lines were obtained. Activation parameters were calculated and are shown in Table 1.

TABLE 1. RATE CONSTANTS OF THE REACTION BETWEEN *p*-TOLUENESULFINIC ACID AND DIPHENYLDIAZOMETHANE IN VARIOUS SOLVENTS

Solvent	Temperature (°C)	k (l mol^{-1}sec^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (e.u.)
CH_2Cl_2[a)]	20.0	300		
Benzene[a)]	20.0	22		
CH_3CN	20.0	4.9		
Ethanol	20.0	1.6		
Dioxane	34.5 30.0 24.8 19.5	0.419 0.321 0.190 0.314	13.0	−18.1
	20.0[b)]	0.19		
DMSO	35.0 30.0 27.0 19.0	0.103 0.0708 0.0570 0.0328	13.0	−23.6

a) Reaction was rapid, and measurements were not so accurate.

b) By the rate of evolution of nitrogen.

Since the reaction between I and II yields nitrogen quantitatively, the rates of the reaction can be determined from the rates of evolution of nitrogen in the solvents in which the reaction rates are not so great. Although the measurements are not very accurate because of the rapidity of the reaction, the rate constant determined is in fair agreement with the value obtained spectrophotometrically.

The reaction between I and II is a three-step reaction, the first step being probably the rate-determining one.

$$ArSO_2H + Ph_2CN_2 \longrightarrow [Ph_2CHN_2^{\oplus}ArSO_2^{\ominus}] \quad (1)$$

$$[Ph_2CHN_2^{\oplus}ArSO_2^{\ominus}] \longrightarrow [Ph_2CH^{\oplus}ArSO_2^{\ominus}] + N_2 \quad (2)$$

$$[Ph_2CH^{\oplus}ArSO_2^{\ominus}] \longrightarrow Ph_2CHO_2SAr \quad (3)$$

The first step is the protonation of I. Since protonations are usually very rapid, it is doubtful whether or not step (1) is really the rate-determining step. Therefore, $CH_3C_6H_4SO_2D$ was synthesized. When the rate of the reaction between $CH_3C_6H_4SO_2D$ and I was determined in dioxane, measurements were not reproducible because the moisture in air dissolves into the dioxane and the H–D exchange takes place rapidly between $CH_3C_6H_4SO_2D$ and water. The measurements were therefore carried out in dioxane containing 2 vol% of heavy water (or ordinary water). The rates were determined by use of both the absorption at 525 nm and the volume of the nitrogen evolved. Table 2 shows that the rates with the deuterated com-

TABLE 2. RATES OF REACTION BETWEEN Ph_2CN_2 AND $C_7H_7SO_2D$ (OR $C_7H_7SO_2H$) IN DIOXANE CONTAINING 2 vol % D_2O (OR H_2O)

Acid	Temp. (°C)	k (l mol^{-1}sec^{-1})	Method[a)]	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (e.u.)
$C_7H_7SO_2D$	29.5 19.8 15.0	0.148 0.0666 0.0478	S S S	12.8	−18.5
	15.0	0.048	V		
$C_7H_7SO_2H$	29.5 19.5 15.0	0.435 0.207 0.142	S S S	14.0	−16.8
	15.0	0.15	V		

a) S=spectrophotometric, V=volumetric.

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1) Organic sulfur compounds, Part 39.

2) F. Arndt and A. Scholz, *Ann. Chem.*, **510**, 70 (1934).

3) Houben-Weyl, "Methoden der organischen Chemie," Bd. IX, pp. 231, 333, Georg Thieme Verlag, (1955).

4) M. Kobayashi, This Bulletin, **39**, 1296 (1966); M. Schank, *Ann. Chem.*, **714**, 117 (1968).

5) J. C. Meek and J. S. Fowler, *J. Org. Chem.*, **33**, 3422 (1968).

TABLE 3. KINETIC ISOTOPE EFFECTS IN THE REACTION BETWEEN Ph_2CN_2 AND $C_7H_7SO_2H$

Reaction temperature (°C)		29.5	19.8	15.0
k_H/k_D	Spectrophotometrically	2.9	3.1	3.3
	Volumetrically			3.2

pound are considerably smaller than those with the ordinary sulfinic acid. The kinetic isotope effects (Table 3) were about 3.0. These data show that protonation of I is the rate-determining step; that is, step (2) is faster than step (1). Step (2) proceeds very readily because it yields the resonance-stabilized diphenylmethyl cation.

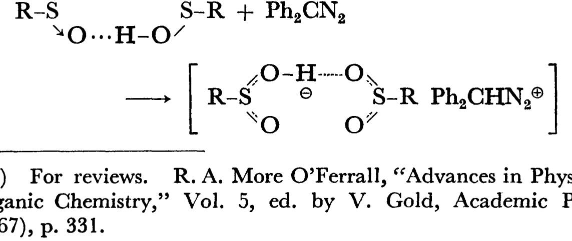
Rates of reaction in dioxane containing 2 vol% water are greater than those in anhydrous dioxane. This is probably due to the increase of the extent of ionization of II by the addition of water.

Reactions between carboxylic acids and aliphatic diazo compounds have been investigated extensively.[6] The reaction between benzoic acid and diphenyldiazomethane in ethanol is of second order, and k (20°C) is 6.6×10^{-3} $M^{-1}sec^{-1}$, $\Delta H^{\neq}=15.6$ kcal mol^{-1}, $\Delta S^{\neq}=-15$ e.u.[7] The rates with II shown in Table 1 are far greater than this value. This might be ascribed to the greater dissociation constant of II in comparison with that of benzoic acid.[8] Kinetic isotope effects were observed in the reaction between carboxylic acids and I (with benzoic acid, $k_H/k_D=3.6$ at 35.35°C in ethanol),[9] showing that protonation of I is the rate-determining step. It is of interest that the values of the kinetic isotope effects with carboxylic acids are approximately the same as those with II.

It was reported that the addition of water increased the rates of reaction between carboxylic acids and I in ethanol.[10]

As shown in Table 1, the reaction rates in non-polar solvents are much greater than those in polar solvents. Similar phenomena were observed in the rates of the reactions of carboxylic acids with I.[9]

The greater rates in non-polar solvents can be rationalized as follows. Infrared spectroscopy shows that sulfinic acids exist as dimers or polymers in non-polar solvents or in crystalline state.[11] When such dimeric sulfinic acids react with I, protonation takes place easily, because the sulfinate anion formed is stabilized by association with another sulfinic acid molecule.



In polar solvents, sulfinic acid molecules lose their dimeric structure and are solvated by solvent molecules. When such solvated molecules are to react with I, the bond between II and a solvent molecule must be cleaved first. This process requires extra energy, and therfore the reaction with I is slower.

Product Studies. In solvents other than alcohols, benzhydryl *p*-toluenesulfinate and benzhydryl *p*-tolyl sulfone were formed in 80—100% yields. The ratio between them varied with the solvent used. Amounts of the products were determined by use of infrared absorptions at 900 and 1140 cm^{-1} (ester) and 1310 cm^{-1} (sulfone) and NMR absorptions. In the reaction in ethanol, benzhydryl ethyl ether was found in addition to the sulfinate and sulfone. The molar ratios of the products in various solvents are shown in Table 4.

TABLE 4. MOLAR RATIOS OF THE PRODUCTS IN VARIOUS SOLVENTS

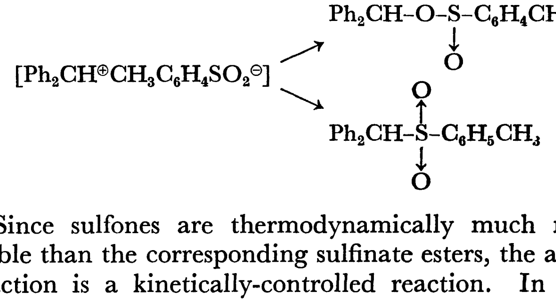
Solvent	Sulfinate[a]	Sulfone[b]	Ether[c]	Total yield (mol %)
CH_2Cl_2	0	100		80
Benzene	20	80		96
CH_3CN	81	19		100
Ethanol	60	14	26	100
Dioxane	83	17		100
DMSO	100	0		82

a) *p*-$CH_3C_6H_4SO_2CHPh_2$.
b) *p*-$CH_3C_6H_4SO_2CHPh_2$.
c) $C_2H_5OCHPh_2$.

In ethanol, the ratio (Sulfinate+Sulfone)/Ether was nearly constant when the concentrations of I and II were varied in the range 2.4—64.0×10^{-3} M.

In DMSO, only benzhydryl *p*-toluenesulfinate was formed in the earlier period of the reaction, but the sulfinate slowly isomerized to sulfone, and the molar ratio of these two products was about 50:50 after 30 min at room temperature.

Reaction (3) is alkylation of the sulfinate anion by diphenylmethyl cation. Since the reactivity of resonance-stabilized diphenylmethyl cation is much less than that of a simple alkyl cation, not only the sulfinate ester but also the sulfone were formed.



Since sulfones are thermodynamically much more stable than the corresponding sulfinate esters, the above reaction is a kinetically-controlled reaction. In such polar solvents as DMSO, the benzhydryl ester once formed redissociates to an ion pair, which recombines, forming the sulfone. Thermal isomerization of a sulfinate ester to a sulfone has been reported on.[12] It is

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[6] For reviews. R. A. More O'Ferrall, "Advances in Physical Organic Chemistry," Vol. 5, ed. by V. Gold, Academic Press (1967), p. 331.

[7] K. Bowden, A. Buckley, N. B. Chapman, and J. Shorter, *J. Chem. Soc.*, **1964**, 3330.

[8] The pK_a value of benzoic acid is 4.6, and that of *p*-toluenesulfinic acid is 1.24 (C. D. Ritchie, J. D. Saltiel, and E. S. Lewis, *J. Amer. Chem. Soc.*, **83**, 4601 (1961)).

[9] R. A. More O'Ferrall, W. K. Kwok, and S. I. Miller, *ibid.*, **86**, 5553 (1964).

[10] J. D. Roberts, W. Watanabe, and R. E. McMahon, *ibid.*, **73**, 760 (1051).

[11] S. Detoni and D. Hadzi, *J. Chem. Soc.*, **1955**, 3163.

[12] D. Darwish and E. A. Preston, *Tetrahedron Lett.*, **1964**, 113.

also known that hydrolysis of benzhydryl sulfinate forms the corresponding sulfone as a byproduct.[13]

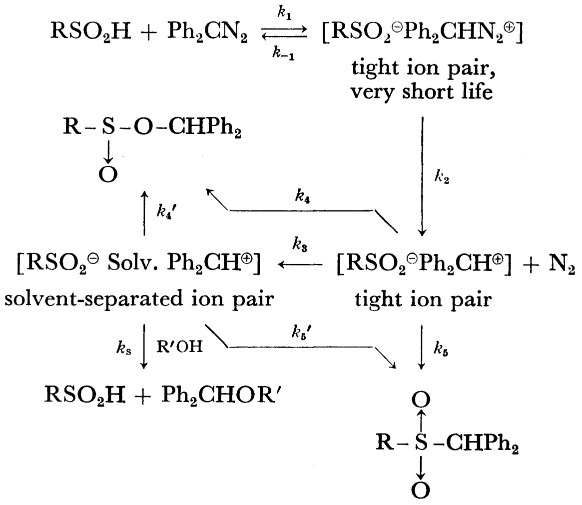
Table 4 shows that in polar solvents the yields of the sulfinate are greater whereas in non-polar solvents those of the sulfone are greater. This is probably related with the fact that rates of the reaction between I and II are smaller in polar solvents and greater in non-polar solvents. A plausible explanation for this phenomenon is as follows. As described above, sulfinic acids exist as dimers or polymers in non-polar solvents. When such dimeric acid reacts with I, the sulfinate anion formed exists in association with another sulfinic acid molecule. Since the negative charge on this dimer anion is not on a specific oxygen atom, combination of diphenylmethyl cation with the oxygen atom of the dimer anion takes place slowly, and consequently the combination with the sulfur atom takes place relatively rapidly.

In such polar solvents as DMSO and dioxane, sulfinic acid molecules are hydrogen-bonded with solvent molecules and the reaction with I is slow. However, since the sulfinate anions formed are not much solvated, they quickly combine with cations at the negatively charged oxygen atoms, forming the thermodynamically less stable benzhydryl sulfinate as the main product.

In ethanol, benzhydryl ethyl ether was formed in a 26% yield which did not change much when the initial concentrations of I and II were varied. Formation of this ether can be ascribed to the attack of ethanol to the ion pair $Ph_2CH^{+-}O_2SC_7H_7$ or the solvent-separated ion pair.

When benzoic acid and I were let to react in ethanol, benzhydryl ethyl ether was found in a 45% yield.[10] When 2,4-dinitrophenol and I were let to react in ethanol, benzhydryl ethyl ether was found in a 39% yield.[14] The smaller yield of this ether in the reaction of I and II in ethanol means that the combination of $C_7H_7SO_2^-$ with Ph_2CH^+ is much faster than the combination of ethanol with Ph_2CH^+. This fact suggests that the ion pair $Ph_2CH^{+-}O_2SC_7H_7$ is tighter than $Ph_2CH^{+-}O_2CR$ and that the sulfinate anion is more nucleophilic than carboxylate anions.

The reaction between I and II can be expressed in the following scheme.



The life time of the ion pair $RSO_2^-Ph_2CHN_2^+$ must be very short, and a molecule of nitrogen is quickly lost from the tight ion pair. Probably k_1 is much smaller than k_2, and k_{-1} is also very small in comparison with k_2. The sulfinate and sulfone are formed mainly from the combination of the tight ion pair $RSO_2^-Ph_2CH^+$, but part of them must arise from the combination of the solvent-separated ion pair, especially in polar solvents. In ethanol, part of the solvent-separated ion pair reacts with ethanol, forming benzhydryl ethyl ether.

Experimental

Materials. Diphenyldiazomethane, produced by oxidation of benzophenone hydrazone with mercuric oxide, was recrystallized from *n*-hexane; mp 31—32 °C.[15] Benzhydryl *p*-toluenesulfinate was synthesized by condensation of the corresponding acid and alcohol in the presence of dicyclohexylcarbodiimide;[16] mp 79 °C.

Kinetic Measurements. Reaction was followed by the decrease of the absorption of I at 525 nm with a Hitachi EPS-3T spectrophotometer. Neither II nor the reaction products had absorptions in this region. Rates of reaction were also determined volumetrically by use of a gas buret.

Reaction Products. The products of the reaction were separated by recrystallization or column chromatography, and identified by NMR and IR. The ratios of the products in the reaction mixture were determined by use of NMR (δ 3.65, $C_7H_7(SO)OCHPh_2$; δ 4.70, $C_7H_7(SO_2)CHPh_2$; δ 6.3—6.7, $CH_3CH_2OCHPh_2$), and IR (ν_{S-O} 1140 and ν_{C-O} 900 cm^{-1} of sulfinate; ν_{S-O} 1310 cm^{-1} of sulfone). Deuterated solvents (such as dimethyl sulfoxide-d_6) were used whenever necessary for NMR measurements.

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