0.22 mol) in 20 ml of DMSO was added at a rate sufficient to maintain the temperature below 40°. After addition was complete, the mixture was allowed to stir under nitrogen at ambient temperature for 2 hr. The reflux condenser was replaced by a distilling head and the reaction flask heated in an oil bath with the bath temperature gradually increased to 110° while material boiling up to 80° was collected. Redistillation through an 8-in. tantalum spiral column into a dry ice–acetone cooled receiver afforded 17.2 g (95%) of *tert*-butylacetylene, bp 36.5–38.5° (lit.[1] bp 36.4–37.8°) identical by ir, nmr, and vpc with an authentic sample prepared by the method of Bartlett and Rosen.[1]

**Registry No.**—**1**, 917-92-0; **2**, 594-84-3; *t*-BuOK, 865-47-4.

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(4) Insufficient care in maintaining efficient stirring and adequate temperature control is responsible for the fluctuating yields frequently observed in the preparation of the sensitive pinacolone dichloride (**2**) which undergoes facile monodehydrochlorination to the corresponding vinyl chloride. However, the vinyl chloride by-product can be used with equal success in the above procedure. In fact, we have frequently used mixtures of the vinyl chloride and dichloride to afford an overall yield of 70–75% of **1** from pinacolone.

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## Leaving Group Effect in the Reaction of 2-Thiophenesulfonyl Halides with Anilines in Methanol

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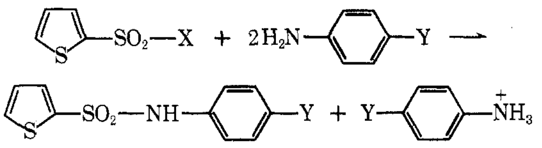
Previously the reaction kinetics of 2-thiophenesulfonyl chloride with several substituted anilines[1,2] was investigated and a study on the ultraviolet and infrared spectroscopic behavior of 2-thiophenesulfonanilides, reaction products, was carried out.[3]

The results of the kinetic measurements showed that 2-thiophenesulfonyl chloride is less reactive than the corresponding benzene derivative,[4] probably owing to the greater conjugative effect of the thiophene ring, but they gave no useful indications about the reaction mechanism.

The Hammett and Brϕnsted coefficient values for 2-thiophenesulfonyl chloride reactions with anilines in methanol[1] are almost coincident to those for the analogous reactions of benzenesulfonyl chloride.

For the latter reaction have been proposed both a one-step synchronous process, S$_N$2,[4] and a two-step addition–elimination mechanism involving the formation of a metastable intermediate, S$_A$N.[5]

In order to give a further contribution to this question, in this paper we report a kinetic study on the leaving group effect in the reaction of 2-thiophenesulfonyl halides with aniline and *p*-anisidine, eq 1.



(1)

X = Cl, Br, F; Y = H, OCH$_3$

### Results and Discussion

The reaction of 2-thiophenesulfonyl halides with a large excess of aniline or *p*-anisidine in methanol solution is pseudo-first-order with respect to the sulfonyl halide. It was followed potentiometrically by titration of the acid produced with sodium hydroxide (see Experimental Section).

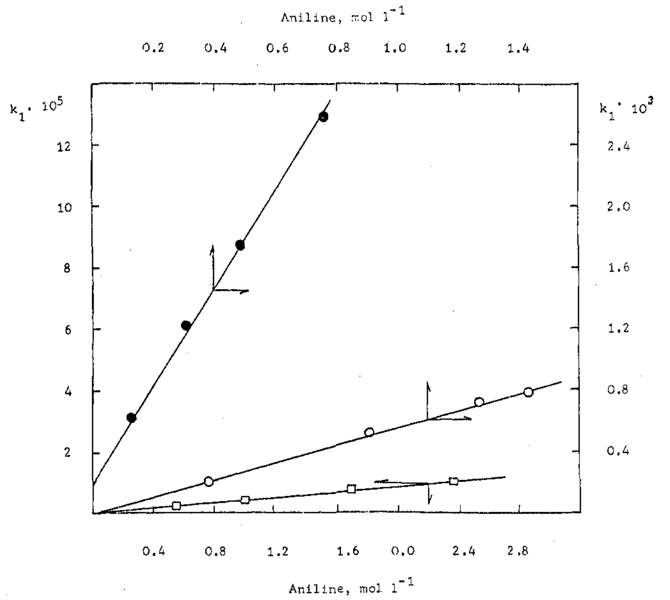


**Figure 1.** Pseudo-first-order rate constants at 25° against aniline concentration for the reaction of 2-thiophenesulfonyl halides: ●, 2-thiophenesulfonyl bromide; ○, 2-thiophenesulfonyl chloride; □, 2-thiophenesulfonyl fluoride.

The reaction of 2-thiophenesulfonyl bromide was followed to at least 80% completion, while that of 2-thiophenesulfonyl fluoride was followed to 25% completion, since it is very slow. The reaction yielded sulfonanilides, since the solvolysis of 2-thiophenesulfonyl halides in methanol is negligible.

Pseudo-first-order rate constants against aniline concentrations give linear plots, indicating that the reaction is first order also with respect to aniline (Figure 1).

The reactions were studied at different temperatures and the second-order rate constants, reported in Table I, together with the standard deviations and the linear correlation coefficients, were obtained by eq 2,[6] using the least-squares method.

$$k_{\mathrm{psl}} = k_{\mathrm{solv}} + k_2[\mathrm{aniline}] \qquad (2)$$

The value of $k_{\mathrm{solv}}$ is almost null for the reactions of 2-thiophenesulfonyl fluoride and chloride and negligible, with respect to $k_2$, for that of 2-thiophenesulfonyl bromide (Figure 1).

The activation parameters are reported in Table II, together with the linear correlation coefficients and the standard deviations.

2-Thiophenesulfonyl bromide reacts *ca.* five times faster than 2-thiophenesulfonyl chloride[1] with both aniline and *p*-anisidine, and respectively *ca.* 7200 and 35,700 times faster than 2-thiophenesulfonyl fluoride. The observed rate sequence follows the halogen polarizability sequence (Br > Cl ≫ F) and is inverse with respect to the S–Hal bond energy sequence.[7]

In order to distinguish between S$_N$2 and S$_A$N mechanisms we determined the relative amount of bond formation and bond breaking, respectively, for S–N and S–Hal bonds in the transition state, using the Brϕnsted coefficients[8] obtained from the plots of log $k_2$ against the p$K_a$ of protonated anilines and hydrogen halides ones (Figure 2).

The Brϕnsted coefficient values ($\beta$) for the leaving group for the reactions of 2-thiophenesulfonyl halides are −0.31 and −0.38, respecitvely, with aniline and *p*-anisidine. The $\beta$

### Table I
### Second-Order Rate Constants for the Reaction of 2-Thiophenesulfonyl Halides with Aniline and *p*-Anisidine in Methanol

| $C_4H_3SSO_2X$ X = | $H_2NC_6H_4Y$ Y = | Temp, °C | $k_2$, l. mol$^{-1}$ sec$^{-1}$ | $r^a$ | No. of runs |
|---|---|---|---|---|---|
| F[c] | H[d] | 25 | $0.4250 \pm 0.044^b \times 10^{-5}$ | 0.995 | 4 |
| F | H | 35 | $1.036 \pm 0.027 \times 10^{-5}$ | 0.999 | 3 |
| F | H | 45 | $2.543 \pm 0.249 \times 10^{-5}$ | 0.995 | 3 |
| F | $OCH_3$[e] | 25 | $0.4629 \pm 0.046 \times 10^{-5}$ | 0.995 | 4 |
| F | $OCH_3$ | 35 | $1.056 \pm 0.101 \times 10^{-5}$ | 0.995 | 3 |
| F | $OCH_3$ | 45 | $2.469 \pm 0.320 \times 10^{-5}$ | 0.992 | 3 |
| Br[f] | H | 15 | $1.370 \pm 0.098 \times 10^{-2}$ | 0.997 | 3 |
| Br | H | 25 | $3.063 \pm 0.064 \times 10^{-2}$ | 0.999 | 4 |
| Br | H | 30 | $4.274 \pm 0.366 \times 10^{-2}$ | 0.996 | 3 |
| Br | H | 35 | $5.338 \pm 0.435 \times 10^{-2}$ | 0.997 | 3 |
| Br | $OCH_3$ | 15 | $9.802 \pm 1.138 \times 10^{-2}$ | 0.987 | 4 |
| Br | $OCH_3$ | 25 | $16.53 \pm 1.48 \times 10^{-2}$ | 0.988 | 5 |
| Br | $OCH_3$ | 35 | $28.27 \pm 0.96 \times 10^{-2}$ | 0.999 | 3 |

[a] *r* = linear correlation coefficient. [b] Standard deviations. [c] Registry no. 382-99-0. [d] Registry no. 62-53-3. [e] Registry no. 104-94-9. [f] Registry no., 52259-99-1.

### Table II
### Activation Parameters for the Reaction of 2-Thiophenesulfonyl Halides with Aniline and *p*-Anisidine in Methanol

| $C_4H_3SSO_2X$ X = | $H_2NC_6H_4Y$ Y = | $r^a$ | $E_A$, kcal mol$^{-1}$ | Log *A* | $-\Delta S^*$, cal mol$^{-1}$ °K$^{-1}$ |
|---|---|---|---|---|---|
| F | H | 0.998 | $15.7 \pm 1.0^b$ | $6.2 \pm 0.7^b$ | $32 \pm 3^b$ |
| F | $OCH_3$ | 0.999 | $15.8 \pm 0.4$ | $6.2 \pm 0.3$ | $32 \pm 1$ |
| Cl[c,d] | H | 0.999 | $12.6 \pm 0.1$ | $7.0 \pm 0.1$ | $28.5 \pm 0.5$ |
| Cl[c] | $OCH_3$ | 0.999 | $9.3 \pm 0.1$ | $5.4 \pm 0.1$ | $35.8 \pm 0.5$ |
| Br | H | 0.995 | $12.2 \pm 0.8$ | $7.4 \pm 0.6$ | $27 \pm 3$ |
| Br | $OCH_3$ | 0.999 | $9.4 \pm 0.2$ | $6.1 \pm 0.2$ | $33 \pm 1$ |

[a] *r* = linear correlation coefficient. [b] Standard deviations. [c] Reference 1. [d] Registry no., 16629-19-9.

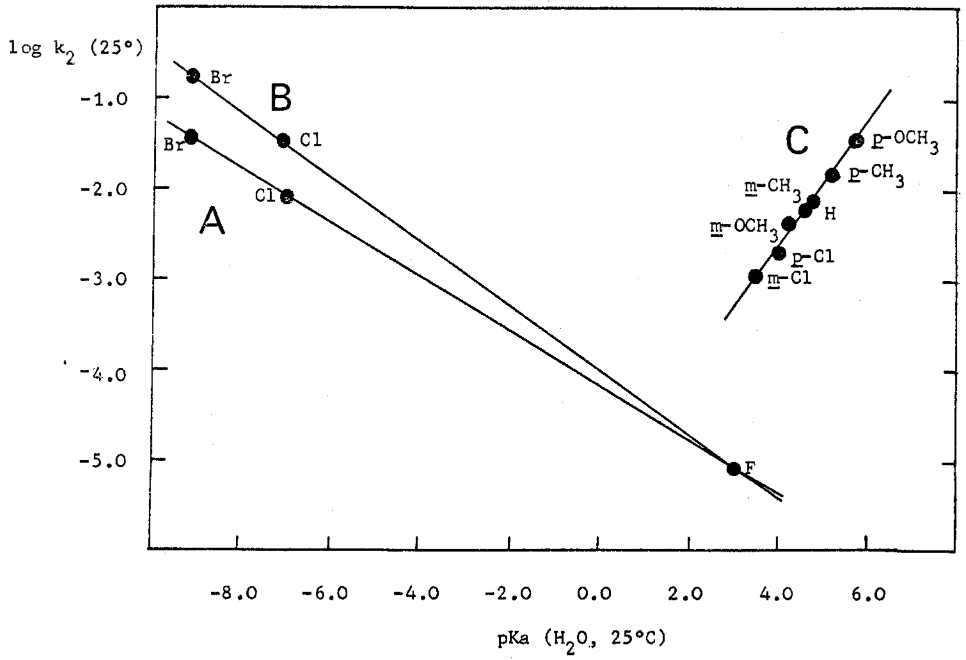


**Figure 2.** Brønsted plots: A, 2-thiophenesulfonyl halides with aniline, $\beta = -0.31$; B, 2-thiophenesulfonyl halides with *p*-anisidine, $\beta = -0.38$; C, 2-thiophenesulfonyl chloride with meta- and para-substituted anilines, $\beta = +0.79$.

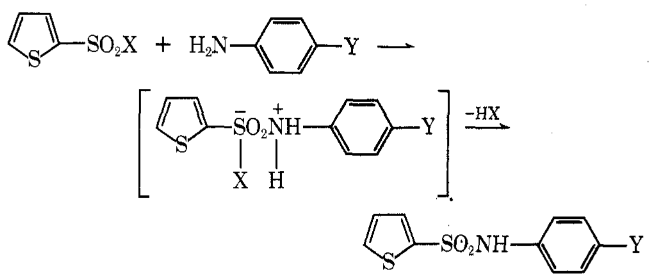
value for the entering nucleophiles, obtained for the reactions of 2-thiophenesulfonyl chloride with some meta- and para-substituted anilines,[1] is +0.79. The comparison between the $\beta$ values suggests a greater degree of S–N bond formation in the transition state with respect to S–Hal bond breaking. This finding implies the formation of an intermediate complex along the reaction path. Nevertheless the Brønsted coefficients must be regarded, as a simple mechanism criterion, with great caution owing to the nonhomogeneous comparison between log $k_2$ and p$K_a$,[9] since the rate constants were measured in methanol solution, while the p$K_a$ values for anilines and hydrogen halides were determined in aqueous solution. The p$K_a$ values reported for hydrogen halides, besides, are rather uncertain.[10]

A further interesting result is that the rates and the activation parameters for 2-thiophenesulfonyl fluoride reactions are almost equal with aniline and *p*-anisidine; this suggests that the rate-determining step is the S–F bond breaking in the transition state.

For the reactions of 2-thiophenesulfonyl chloride and bromide, instead, the rate-determining step is the nucleophilic attack to the sulfonyl halide. In fact the reaction rates (Table I) and the activation energies (Table II) are affected by the basicity of the nucleophilic reagent and not by the leaving halogen nature.

In conclusion the data on the reactivities of 2-thiophenesulfonyl halides and the relative activation parameters could fit well with a two-step addition–elimination mechanism $S_{AN}$, the rate-determining step being the S–N bond formation for 2-thiophenesulfonyl chloride and bromide and the S–F bond breaking for sulfonyl fluoride (see Scheme I).

Scheme I



## Experimental Section

**Materials. 2-Thiophenesulfonyl chloride** was obtained by adding at 20°, under stirring, 33.6 g (0.4 mol) of thiophene to a mixture containing 66 ml (1 mol) of chlorosulfonic acid and 83 g (0.4 mol) of phosphorus pentachloride, following the procedure already described,[11] 70% yield, bp 92–93° (1 mm), mp 31–32° from petroleum ether (bp 30–60°).

**2-Thiophenesulfonyl Fluoride.** To an aqueous solution (30 ml) containing 7.4 g (0.2 mol) of ammonium fluoride, 18.3 g (0.1 mol) of 2-thiophenesulfonyl chloride was added. The mixture was refluxed for 5 hr, then treated with warm water and extracted with ether. The evaporated extract gave the products, 90% yield, bp 75–76° (1 mm).[12]

**2-Thiophenesulfonyl Bromide.** This product was synthesized using the method reported for benzenesulfonyl bromide.[13]

To 10.7 g (0.06 mol) of 2-thiophenesulfonyl hydrazide (see later) in 200 ml of 10% hydrochloric acid was added at 20° an aqueous solution (35 ml) containing 2.4 g (0.02 mol) of potassium bromide and 6.7 g (0.04 mol) of potassium bromate. The precipitate was filtered quickly, washed with cold water, and dried *in vacuo*, 60% yield, mp 48–49° from petroleum ether.

*Anal.* Calcd for $C_4H_3BrO_2S_2$: Br, 35.19. Found: Br, 35.28.

**2-Thiophenesulfonyl hydrazide** was synthesized by the method reported for benzenesulfonyl hydrazide.[14]

To 12.5 g (0.25 mol) of 85% hydrazine hydrate in 30 ml of ether was added an ether solution (30 ml) containing 18.3 g (0.1 mol) of 2-thiophensulfonyl chloride. The mixture was stirred for 30 min and the precipitate was collected and washed with cold water, 60% yield, mp 68–69° from water.

*Anal.* Calcd for $C_4H_6N_2O_2S_2$: N, 15.72. Found: N, 15.60.

Aniline and *p*-anisidine were commercial products purified by several distillations or crystallizations.

Methanol (R. S. Carlo Erba) was used throughout; no special purification was undertaken, since several experiments showed that elaborate purification was unnecessary.

**Kinetic Procedure.** Rate measurements were done by a digital pH meter, Amel Model 333, equipped with a motorized burette, Amel Model 233, by continuous titration of the acid produced with 0.1 *N* sodium hydroxide, following the procedure described before.[1] The reagent concentrations ranged from *ca.* 0.0003 to *ca.* 0.013 mol for 2-thiophenesulfonyl halides and from *ca.* 0.004 to *ca.* 2 mol for the anilines, depending on the reaction rates.

The first-order rate constants were obtained from the slope of conventional plots of log $(a - x)$ against time, using the least-squares method. The activation energies were calculated from the Arrhenius equation by the least-squares method. The entropies of activation were computed for 25°, using the suitable equation.

**Product Analysis.** Methanol solutions of 2-thiophenesulfonyl halide (0.025 mol) and aniline or *p*-anisidine (0.15 mol) were allowed to react at room temperature until completion. Methanol was evaporated, and then the residue was treated with aqueous 40% sodium hydroxide and extracted twice with ether or filtered. The aqueous layer was acidified and the precipitate was collected, washed with water, and crystallized from aqueous ethanol: 2-thiophenesulfonanilide, mp 99–100[1]; 2-thiophene-4′-methoxysulfonanilide, mp 104°.[1]

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**Registry No.**—Thiophene, 110-02-1; chlorosulfonic acid, 7990-94-5; 2-thiophenesulfonyl hydrazide, 52260-00-1.

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# Model Studies of Terpene Biosynthesis. Synthesis and Absolute Configuration of (+)-*trans*-2,2-Dimethyl-3-(2′-methylpropenyl)cyclobutanol[1]

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Several mechanisms have been suggested for the head-to-head rearrangement of presqualene and prephytoene