

전이 상태의 변이 모형에 대한 제한성(1) 염화 메시틸렌 술폰의 가용매 분해 반응에 대한 이중통로

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Limitation of the Transition State Variation Model (I) Dual Reaction Channels for Solvolyses of Mesitylenesulphonyl Chloride

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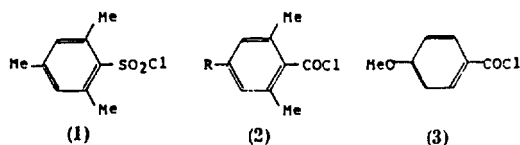
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The possibility that mechanistic changes occur by varying contributions from two competing reaction channels is not currently favoured;¹ *e. g.*, S_N2 and S_N1 reactions are now regarded as extremes within a single mechanistic spectrum, including reactions proceeding *via* "exploded" S_N2 transition state having high cationic character.² Mechanistic changes occur through a spectrum of transition state variations, usually (but not necessarily³) within a single reaction channel. These changes can be shown on potential energy contour diagrams, and may include perturbations both in the direction of, and perpendicular to, the reaction coordinate.^{3, 4} As the popularity and versatility of this approach have increased, it has become increasingly difficult to establish examples of mechanistic changes *via* competing reaction channels. We now report that complex variations in the rates and products of solvolyses of

mesitylenesulphonyl chloride (1) in aqueous alcohols can be explained by changes in contributions from two simultaneous reaction channels. Also a region of solvent composition, at which a very unusual reversal of a trend in product selectivity occurred, was predicted solely from rate data.



Our work on solvolyses of (1) is an extension of studies of both sulphonic⁵ and carboxylic acid chlorides.⁶ Logarithms of rate constants for solvolyses of mesityl chloride (2, R=Me) and 2,6-dimethylbenzoyl chloride (2, R=H) plot linearly (slope = 0.84) *vs.* rate constants for *p*-methoxybenzoyl chloride (3), with very little dispersion into separate correlation lines for different aqueous binary mixtures (*e. g.*, with acetone, ethanol and methanol cosolvents).^{6a} Product selec-

* In commemoration of the 60th Birthday.

Table 1. S. Values (eq. 1) for solvolyses of mesitylenesulphonyl chloride(1) in alcohol/water (%v/v) mixtures at 25 °C

Composition	95	90	80	70	60	50	40	30	20	10	5
Ethanol	0.8	1.5	2.5	3.0	3.8	4.1	4.6	3.4	3.1	1.7	1.3
Methanol	1.1	1.9	2.4	3.2	3.6	3.9	4.4	4.5	3.9	3.5	3.3



Fig. 1. Correlation of logarithms of rate constants for solvolyses of mesitylenesulphonyl chloride (1) vs. logarithms of rate constants for solvolyses of *p*-methoxybenzoyl chloride (3) at 25 °C; solvent codes: A = % v/v acetone/water, E = % v/v ethanol/water, M = % v/v methanol/water.

tivities (*S*, equation 1) are independent of solvent composition. Also, *S*, eq. 1, for ethanol/water mixtures consistent with product formation by collapse of a solvent-separated ion pair.^{6a}

$$S = \frac{([\text{ester product}] [\text{water solvent}])}{([\text{acid product}] [\text{alcohol solvent}])} \quad (1)$$

A comparison of solvolyses of (1) with solvolyses of (3) is shown in the Fig. These results showed marked dispersions into separate correlation lines for the three binary aqueous solvents, and pronounced changes in slopes for acetone/water and ethanol water at ca. 40% solvent compositions. Detailed inspection of the plots revealed another change in slope between lines for 40M–20 M and 20 M–water, approximately coinciding with the lowering of *S* from 4, 5 in 30 M to 3.9 in 20 M (only these *S* values and those or less aqueous methanol/water mixtures were known at this stage). This interpretation is strongly supported by additional *S* values (Table 1). Also the trend of increasing *S* values for more aqueous

ethanol/water mixtures reverses at 40% composition, almost exactly the same composition at which there is a change in slope of the rate–rate profile (see Fig. 1).

From these results we suggest that two competing reaction channels are operating simultaneously. The channel dominant in less aqueous solvents shows an increase in *S* as water is added. The second channel is strongly sensitive to changes in solvent ionizing power, it becomes dominant in more aqueous media and *S* decrease. Because *S* is not constant (cf. similar carboxylic acid chlorides^{6a}), it is unlikely that the second channel is purely *S*₁.^{7, 8} A change in rate limiting step within one reaction channel is excluded because two product determining steps are required to explain the sharp reversal of trend in *S*.

Further work is currently in progress. Similar studies of rates and products of solvolyses of *p*-substituted benzoyl chlorides have recently been analysed quantitatively in terms of competing reaction channels.⁹

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