Elimination–Addition. Part X.[1] Rates of Addition of Amines to *p*-Toly Vinyl Sulphone

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Reactivities of amines in additions to *p*-tolyl vinyl sulphone have been determined in competitive reactions (in benzene) and by individual rate measurements (in benzene and in alcohols).

Reactivities are much more sensitive to the steric requirements of the amine than to its basicity. In ethanol, primary amines are less reactive than secondary amines. This is shown to be due to the greater degree of solvation of the former.

Rates in benzene are much lower than in ethanol and while in both solvents the reaction order with respect to sulphone is unity, the order in amine is second and first, respectively.

A mechanism, which involves concerted formation of the new C–N and C–H bonds in the transition state, is suggested to account for these observations.

NUCLEOPHILIC addition to simple olefins [2] and acetylenes does not normally occur unless a group is attached to the multiple bond which is capable of polarising it sufficiently to encourage the attack of nucleophiles, and of stabilising the transition state for addition. These conditions are satisfied in such familiar reactions as cyanoethylation,[3] nitroethylation,[4] and pyridylethylation.[5] Investigations have also been made of the

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[1] Part IX, C. H. McMullen and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1966, 1221.

[2] S. Patai and Z. Rappoport in "The Chemistry of Alkenes," ed. S. Patai, Interscience, New York, 1964.

[3] P. K. Butskus, *Russ. Chem. Rev.*, 1961, **30**, 583; 1962, **31**, 283.

[4] M. B. Frankel, *J. Org. Chem.*, 1958, **23**, 813; L. Zeldin and H. Schechter, *J. Amer. Chem. Soc.*, 1957, **79**, 4708.

[5] R. Levine and M. H. Wilt, *J. Amer. Chem. Soc.*, 1952, **74**, 342.

additions of amines to αβ-unsaturated ketones,[6,7] esters,[8,9] and acids [10] but in spite of much synthetic application of this type of reaction, very little information is available on their mechanisms. Those reactions which have been studied in any detail and tested in this respect are reversible under the reaction conditions. These include the Michael reaction,[11] cyanoethylation,[12] and additions to a variety of substrates particularly polycyano-olefins.[13] In addition, amine-catalysed isomerisations of geometric olefin isomers have been reported.[14,15] These similarly involve reversible nucleophilic addition to an activated double bond.

To obtain a clear mechanistic picture of such reactions, it is desirable to determine the stoicheiometry and order of the reaction with respect to each component, the effect of variation in solvent, and the effect of nucleophile and olefin structure upon the rate of the reaction. In previous Parts we have examined the products obtained from the addition of amines to both alkenyl [16] and alkynyl [17] sulphones. 1,1-Adducts are readily formed in high yields from each type. We now consider the reactivities of a number of amines of differing structural types towards *p*-tolyl vinyl sulphone together with solvent effects upon reaction rates. In Part XI we examine electronic effects upon the reactivity of aryl vinyl sulphones. In Part XII [18] we report on the behaviour of homologues of the vinyl sulphone and upon the reactivity of allenyl and alkynyl sulphones.

Amine Reactivity.—Competitive experiments. Our initial experiments were designed to yield information on the relative reactivities of amines towards *p*-tolyl vinyl sulphone. The method was to allow a twenty-molar excess of a mixture of two amines to react with the sulphone in benzene. Subsequent determination of the amount of each adduct in the binary mixture of adducts thus obtained allowed the relative reactivities of the amines to be calculated. An infrared spectroscopic technique was used for analysis of the adduct mixture and in all cases it was confirmed by separate experiments that high yields (<95%) of adduct were obtained from individual amines. We carried out rigorous tests which showed that additions to *p*-tolyl vinyl sulphone are not reversible under the conditions used, and that the products, therefore, result from kinetically and not thermodynamically controlled reactions. These considerations also apply to reactions discussed in the two following Papers.

The results (Table 1) are divided into two series based on the two selected reference amines, morpholine and 3-methoxypropylamine.

It was not possible to relate the two series together accurately, *i.e.*, to determine a value for $k_{morpholine}/k_{3\text{-methoxypropylamine}}$, but the results show a considerable divergence in reactivity and they are discussed in conjunction with the direct rate measurements.

TABLE 1

Relative reactivities of amines in additions to *p*-tolyl vinyl sulphone

	$\frac{k_{amine}}{k_{morpholine}}$		$\frac{k_{amine}}{k_{3\text{-methoxypropylamine}}}$ (±0·02)		
Pyrrolidine	10·0 ± 1·0	n-Butylamine	1·15	Cyclohexylamine	0·37
Piperidine	7·0 ± 0·7	n-Hexylamine	1·04	Isopropylamine	0·35
3-Methylpiperidine	5·0 ± 0·5	Benzylamine	1·01	s-Butylamine	0·29
N-Methylpiperazine	2·5 ± 0·2	2-Methylpiperidine	0·72	2-Ethylpiperidine	0·099
		Cyclopentylamine	0·70	3-Ethylmorpholine	0·095
		Diethylamine	0·64		

Rate measurements. The difficulty of obtaining accurate data on relative reactivities over the whole range of amines prompted us to use direct rate measurements with, initially, ethanol as the solvent. Two analytical methods (*a*) and (*b*) were employed. These involved, respectively, determination of unchanged sulphone by an adaptation of a special method for electrophilic olefins [19] or determination of unchanged amine by the dithiocarbamate procedure.[20] In all cases, the reactions were of the first order in sulphone and of the first order in amine; second-order rate constants are listed in Table 2.

In order to complement our direct rate measurements in ethanol as solvent, we also briefly studied the effect of a change to benzene as solvent upon both rate and reaction order. The rate was depressed by this change (a factor of 40 being typical) indicating that the transition state is markedly more polar than the reactants. Further the reactions are no longer of first order in amine. The apparent second-order rate constants

[6] N. H. Cromwell, *Chem. Rev.*, 1946, **38**, 83.
[7] R. Baltzly, E. Lorz, P. B. Russell, and F. M. Smith, *J. Amer. Chem. Soc.*, 1955, **77**, 624.
[8] K. L. Mallik and M. N. Das, *Z. phys. Chem.* (*Frankfurt*), 1960, **25**, 205.
[9] A. Vystrcil and S. Hudecek, *Chem. Listy*, 1950, **44**, 262.
[10] M. Lipp, F. Dallacker, and H.-G. Rey, *Chem. Ber.*, 1958, **91**, 2239.
[11] J. Hine and L. A. Kaplan, *J. Amer. Chem. Soc.*, 1960, **82**, 2915.
[12] M. Friedman and J. S. Wall, *J. Amer. Chem. Soc.*, 1964, **86**, 3735.
[13] Z. Rappoport and S. Gertler, *J. Chem. Soc.*, 1964, 1360, and references therein.
[14] Z. Rappoport, C. Degani, and S. Patai, *J. Chem. Soc.*, 1963, 4513.
[15] M. Davies and F. P. Evans, *Trans. Faraday Soc.*, 1955, **51**, 1506.
[16] A. T. Kader and C. J. M. Stirling, *J. Chem. Soc.*, 1962, 3686.
[17] C. J. M. Stirling, *J. Chem. Soc.*, 1964, 5863.
[18] S. T. McDowell and C. J. M. Stirling, *J. Chem. Soc.* (*B*), 1967, 351.
[19] D. W. Beesing, W. P. Tyler, D. M. Kurtz, and S. A. Harrison, *Analyt. Chem.*, 1949, **21**, 1073.
[20] F. E. Critchfield, "Organic Functional Group Analysis," Pergamon Press, Oxford, 1963.

obtained for reactions between *p*-tolyl vinyl sulphone and piperidine, morpholine, and isopropylamine, respectively, are listed in Table 6. These constants change markedly with variation in the initial ratio of amine to sulphone indicating that the reaction is not a simple second-order process. Third-order rate constants were then obtained using the appropriate expression for a reaction of the type:

$$2A + B \longrightarrow AB + A$$

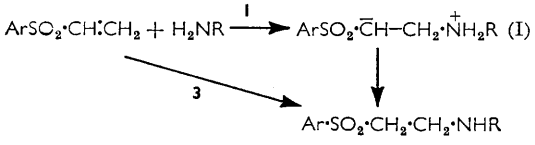
$$viz.,\quad k_3t\,(b-a) = \frac{x}{a(a-x)} + \frac{2{\cdot}303}{(b-a)}\left[\log\frac{b}{a}\cdot\frac{(a-x)}{(b-x)}\right]$$

where $a = [\text{amine}]_{\text{initial}}$ and $b = [\text{sulphone}]_{\text{initial}}$

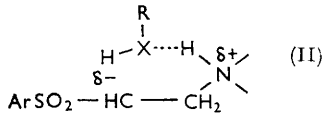
Values of k_3, evaluated graphically from plots of the R.H.S. expression against t, are also listed in Table 6. Provided that the amine is present in excess, the variation in these constants is very much less than in the corresponding second-order constants. Further, for reactions with piperidine and isopropylamine, at least, these variations are random.

We conclude, therefore, that for reactions in benzene the order in amine is 2 (or nearly 2) and we suggest that, in benzene, a second molecule of amine is required in the transition state, which, in ethanol, may be replaced by a solvent molecule. Similar behaviour has been noted [15] for the piperidine-catalysed isomerisation of dimethyl maleate in anisole.

We consider two possibilities for the reaction mechanism:



In pathway (*a*) [reactions (1) and (2)] the intermediate zwitterion (I) is formed which subsequently undergoes proton transfer to yield the final product. It seems certain that, if this were the pathway, step (1) would be rate-controlling. Proton transfers are generally very rapid [21] and in particular proton transfer to α-sulphonyl carbanions is nearly fast enough to be diffusion-controlled.[22] This is supported by the observation that in the addition [23] of thiophenoxide ion to 1-*p*-tolylsulphonylcyclohexene, the less stable [24] *cis* isomer is produced. The second-order dependence on amine for reactions in benzene leads us to reject the two-stage mechanism with stage (1) rate-controlling, as only one molecule of amine need be involved in this step. Instead, we favour a concerted process (3) in which the function of the additional molecule of amine (or ethanol) is in proton transference (II). The order of the reaction



(II)

in ethanol does not exclude pathway (*a*). In the following Paper, however, we describe the determination of the Hammett ρ value (= +1·59) for the reaction. This value is well below the maximum possible value (see p. 349) and we do not, therefore, favour formation of a fully dipolar intermediate as in pathway (*a*). This picture of the transition state is consistent both with the very negative entropies of activation observed [18] and with the great sensitivity of the reaction to the steric requirements of the amine (below). In this connection, it seems certain that the attacking species is the associated amine and not the conjugate base, $\bar{R}NH$ derived from the equilibrium

$$2\,RNH_2 \rightleftharpoons \bar{R}NH + \overset{+}{R}NH_3$$

We find that added tertiary amine does not affect addition rates, and similar conclusions have been reached by Mallik and Das [8] in their study of the additions of amines to acrylates. Other workers have, however, reported basic catalysis in additions of amines to electrophilic olefins.[25]

Three aspects of the series of rate constants for ethanol reactions are striking. First, a very wide

TABLE 2

Second-order rate constants for reactions of amines with *p*-tolylvinyl sulphone in ethanol at 25°

Amine	Method	10^3k (l. mole^{-1} sec.$^{-1}$)	pK_a
Piperidine	*a*	585 ± 2	11·1
Dimethylamine	*a*	451 ± 2	10·8
Morpholine	*a*	33·8 ± 10·3	8·4
Diethylamine	*a*	23·3 ± 0·2	11·0
Di-n-butylamine	*a*	12·5 ± 0·1	11·3
2-Methylpiperidine	*b*	10·9 ± 0·1	11·0
3-Methoxypropylamine	*b*	13·0 ± 0·1	10·0 *
Isobutylamine	*b*	10·8 ± 0·3	10·7
n-Hexylamine	*b*	10·6 ± 0·4	10·6
n-Butylamine	*b*	8·0 ± 0·1	10·6
Cyclopentylamine	*b*	6·60 ± 0·03	10·7
Cyclohexylamine	*b*	4·95 ± 0·15	10·7
Isopropylamine	*b*	4·32 ± 0·04	10·6
s-Butylamine	*b*	4·24 ± 0·07	10·6
2-Ethylpiperidine	*b*	3·78 ± 0·28	†
t-Butylamine	*b*	0·86 ± 0·01	10·7
3-Ethylmorpholine	*b*	0·44 ± 0·02	†
2,6-Dimethylpiperidine	*b*	0·085 ± 0·005	11·1

* Value for 3-hydroxypropylamine. † Lit. value not available.

[21] R. P. Bell, *Quart. Rev.*, 1959, **13**, 169.
[22] R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.
[23] W. E. Truce and A. J. Levy, *J. Amer. Chem. Soc.*, 1961, **83**, 4641.
[24] Cf. F. G. Bordwell and W. A. Hewitt, *J. Amer. Chem. Soc.*, 1957, **79**, 3093.
[25] M. Wronski and J. Bodanski, *Zeszyty Nauk Univ. Lodz*, 1963, **14**, 153 (*Chem. Abs.*, 1965, **62**, 3903).

spread in the reactivities of amines and in particular of cyclic secondary amines, is seen. This is to be attributed mainly to steric effects. Thus piperidine is 7000 times as reactive as its 2,6-dimethyl homologue, and chain-branching in acylic amines lowers reactivity although the effect is less strong. Secondly, provided that the steric requirements of amines are the same, large differences in basicity have relatively little effect on reactivity. [pK_a data in Table 2 are taken from Perrin [26] and refer to aqueous solutions. There is good evidence [27] that *relative* basicities are little affected by a change to alcoholic solvents.] Morpholine, for example, is about one seventeenth as reactive as piperidine but is more than one hundred times less basic. In contrast to these findings, a good correlation between amine basicity and reactivity has been found for isomerisations of maleate esters.[15]

Thirdly, primary amines are notably less reactive than secondary. While, for example, diethylamine is slightly more basic than butylamine, there can be no doubt that, in the absence of solvation, the steric requirements of the secondary amine are greater. The acute sensitivity of the system to non-bonded interactions has already been referred to. It seems probable that a primary amine in ethanol forms hydrogen bonds through both of its *N*-hydrogen atoms,[28,29] while only one such atom is available in secondary amines. The reactivity of the primary amine is thus depressed by its relatively greater bulk (when allowance is made for solvation) together with the need to shed solvent molecules in the transition state.

We have obtained evidence in favour of this view by examining the rates of reactions in t-butyl alcohol. We reasoned that if the greater degree of solvation of primary than secondary amines was responsible for the lower reactivity of primary amines, then, by using a hydrogen-bonding solvent with exacting steric requirements of its own, solvation of both primary and secondary amines might be confined to a single solvating molecule. The effect of this change of solvent upon the reactivities of two primary–secondary amine pairs is shown in Table 3.

TABLE 3

Solvent effects on rates of addition of amines to *p*-tolyl vinyl sulphone at 25·0° (k in l. mole^{-1} sec.$^{-1}$)

Amine	10^3k_{EtOH}	$10^3k_{t\text{-BuOH}}$
Bu^nNH_2	8·0 ± 0·1	14·4 ± 0·2
$n\text{-}C_6H_{13}NH_2$	10·6 ± 0·4	15·8 ± 0·5
$Bu^n{}_2NH$	12·5 ± 0·1	0·59 ± 0·01
Et_2NH	23·3 ± 0·2	1·31 ± 0·02

The rates for secondary amines in t-butyl alcohol are depressed roughly twenty-fold. This is understandable in view of the lower dielectric constant of the medium (EtOH 25; Bu^tOH 10). By contrast, rates of addition of primary amines are increased. Clearly, the depressive effect of a lowering of the dielectric constant of the solvent is more than offset by the beneficial effect of a reduction in the extent of nucleophile solvation. The results of the competitive experiments in benzene also lend weight to these conclusions: n-butylamine, for example, is twice as reactive as diethylamine. Presumably the rather weak association [30] between amine molecules is not sufficient to maintain the differential in reactivities between primary and secondary amines that is found in ethanol.

Within the series of primary amines, the effect of α-branching is much more serious than for β-branching. Thus t-butylamine is very much less and isopropylamine is less reactive than butylamine, but s-butylamine is only slightly less reactive than isopropylamine in competitive experiments. The difference in reactivity between cyclopentylamine and cyclohexylamine reflects the fact that the β-carbon atoms are " tied-back " to a greater extent in the five-membered ring.

Within the series of secondary amines, the marked effect of " tying-back " the α-carbon atoms is shown in the very high reactivities of the cyclic amines when compared with their acyclic analogues. The depressive effect on rate of α-branching is shown in the low reactivity of 2-methylpiperidine, and di-isopropylamine fails to add to the vinyl sulphone in our conditions. Again, β-branching has only a relatively small influence on rate as shown in the results of 2-ethylpiperidine and 3-ethylmorpholine. When the β-carbon is a member of a ring, as in 3-methylpiperidine, the effect of β-branching becomes negligible.

It is of interest to compare our results with reactivities of amines in other reactions. Hall [31] has compiled amine reactivities towards a number of substrates and it emerges that the rates in the present system are much more dependent on nucleophile reactivity in most other systems, particularly those in which nucleophilic displacement at saturated carbon is involved. A comparable relationship between reaction rate and amine structure is found in reactions with 1-chloro-2,4-dinitrobenzene. This similarity emphasises the similarity of mechanism: nucleophilic displacement in 1-chloro-2,4-dinitrobenzene involves initial addition.[32]

EXPERIMENTAL

General.—Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. AnalaR benzene was dried, distilled, and stored over sodium. Ethanol was dried by the magnesium–iodine method.[33] t-Butyl alcohol was distilled five times from sodium. Light petroleum ether had b. p. 40—60° unless otherwise stated. Extracts were dried over anhydrous $MgSO_4$.

Propan-2-ol was freed from aldehydes as follows: the

[26] D. D. Perrin, " Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths, 1965.
[27] H. K. Hall, *J. Phys. Chem.*, 1956, **60**, 63, and references therein.
[28] F. E. Condon, *J. Amer. Chem. Soc.*, 1965, **87**, 4481, 4485.
[29] H. K. Hall, *J. Amer. Chem. Soc.*, 1957, **79**, 5441.
[30] C. C. Pimentel and A. L. McClellan, " The Hydrogen Bond," Freeman, San Francisco, 1960.
[31] H. K. Hall, *J. Org. Chem.*, 1964, **29**, 3539.
[32] J. F. Bunnett, *Quart. Rev.*, 1958, **12**, 1.
[33] A. I. Vogel, " Practical Organic Chemistry," Longmans, Green & Co., London, 1956.

commercial solvent, containing 2—3 g./l. of silver nitrate, was kept in diffuse daylight for 3 weeks. After addition of sodium chloride and filtration, the solvent was fractionated and stored in the dark.

Reagents.—Amines were dried (KOH) and fractionated through a 30 in. helix-packed column operating at a reflux ratio of 50 : 1. Their physical constants were as follows: 3-ethylmorpholine,[34] b. p. 157°, n_D^{25} 1·4502; piperidine, b. p. 106°, n_D^{25} 1·4520; morpholine, b. p. 127°, n_D^{25} 1·4523; diethylamine, b. p. 56°, n_D^{25} 1·3850; di-*n*-butylamine, b. p. 159°, n_D^{25} 1·4153; benzylamine, b. p. 184°, n_D^{25} 1·5385; 2-methylpiperidine, b. p. 117°, n_D^{25} 1·4463; 3-methoxypropylamine, b. p. 120°, n_D^{25} 1·4174; isobutylamine, b. p. 68°, n_D^{25} 1·3940; *n*-hexylamine, b. p. 130°, n_D^{25} 1·4225; n-butylamine, b. p. 77°, n_D^{25} 1·3995; cyclopentylamine, b. p. 107°, n_D^{25} 1·4475; cyclohexylamine, b. p. 134°, n_D^{25} 1·4575; isopropylamine, b. p. 34°, n_D^{20} 1·3753; s-butylamine, b. p. 63°, n_D^{25} 1·3425; 2-ethylpiperidine, b. p. 142°, n_D^{25} 1·4443; t-butylamine, b. p. 45°, n_D^{25} 1·3765; 2,6-dimethylpiperidine, b. p. 128°; *N*-methylpiperazine, b. p. 135°; pyrrolidine, b. p. 88°, n_D^{25} 1·4235. For use in kinetic determinations, ethanolic solutions of amines were standardised by titration against perchloric acid in acetic acid.

p-Tolyl vinyl sulphone had m. p. 65—66° (from ethanol) (lit.,[35] m. p. 65—66°).

Formation of Adducts.—*p*-Tolyl vinyl sulphone (2 g.) and the amine (5 mol.) were allowed to react in benzene (50 ml.) at 25°. After 3 days, the solution was evaporated and distillation of the residue gave the adduct. Details are given in Table 4.

Competitive Experiments.—*p*-Tolyl vinyl sulphone in benzene (25 ml.) was added with vigorous stirring to a solution of two amines in benzene at 25·0° (thermostat), such that the initial concentrations in the mixture were 0·11M in sulphone and 1·1M in each amine. After being kept at 25° for 2 days, the mixture was evaporated and distillation of the residue gave the mixture of adducts. Morpholine, 3-methoxypropylamine, and 3-ethylmorpholine were employed as reference amines because of their suitable reactivities and characteristic infrared spectra. The mixtures of adducts were analysed by matching the spectra of their 7% solutions in benzene with those of binary mixtures of known composition prepared from individual pure adducts. The infrared cells employed were of 0·1 mm. pathlength and were equipped with NaCl windows. Relative reactivities of amines were calculated from the amounts of each adduct in the adduct mixtures. Results are in Table 1.

TABLE 4

Adducts formed from p-tolyl vinyl sulphone and amines

Amine	Yield (%)	B. p.	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
Piperidine	98	163°/0·15 mm.				(Lit.,* b. p. 195—205°/8 mm.)			
Morpholine	95	65 [a]	57·9	6·9	4·8	$C_{13}H_{19}NO_3S$	57·9	7·1	5·2
Ethylamine	98	41—42 [a]	58·1	7·4	6·3	$C_{11}H_{17}NO_2S$	58·1	7·5	6·2
Diethylamine	95	134/0·07 mm.	61·2	8·4	—	$C_{13}H_{21}NO_2S$	61·2	8·2	—
Isopropylamine	97	34 [a]	60·0	8·0	6·1	$C_{12}H_{19}NO_2S$	59·75	7·9	5·8
t-Butylamine	99	61 [a]	61·3	8·2	—	$C_{13}H_{21}NO_2S$	61·1	8·3	—
n-Butylamine	98	160/0·05 mm.	60·9	8·4	5·7	$C_{13}H_{21}NO_2S$	61·1	8·3	5·5
2-Methylpiperidine	99	58—59 [a]	64·2	8·15	5·0	$C_{15}H_{23}NO_2S$	64·0	8·2	5·0
2-Ethylpiperidine	98	27—28 [a]	64·8	8·6	—	$C_{16}H_{25}NO_2S$	65·0	8·5	—
Pyrrolidine	97	64—65 [a]	61·5	7·6	—	$C_{15}H_{23}NO_2S$	61·6	7·6	—
3-Methylpiperidine	97	159/0·08 mm.	64·15	8·35	—	$C_{15}H_{23}NO_2S$	64·0	8·2	—
N-Methylpiperazine	99	75 [a]	59·4	8·0	9·9	$C_{14}H_{22}N_2O_2S$	59·6	7·85	9·9
2,6-Dimethylpiperidine	70	172/0·1 mm.	64·6	8·8	—	$C_{16}H_{25}NO_2S$	65·0	8·5	—
n-Hexylamine	97	159/0·05 mm.	63·9	8·7	4·8	$C_{15}H_{25}NO_2S$	63·6	8·9	4·9
3-Ethylmorpholine	98	57—58	60·75	7·7	4·8	$C_{14}H_{21}NO_3S$	60·6	7·8	4·7
Benzylamine	97	200/0·1 mm.	66·2	6·7	4·9	$C_{16}H_{19}NO_2S$	66·4	6·6	4·8
Cyclopentylamine	97	160/0·01 mm.	63·05	8·1	5·3	$C_{14}H_{21}NO_2S$	62·9	7·9	5·2
Cyclohexylamine	100	170/0·05 mm.	63·9	8·3	4·8	$C_{15}H_{23}NO_2S$	64·0	8·2	5·0
3-Methoxypropylamine	96	162/0·07 mm.	57·6	7·8	5·2	$C_{13}H_{21}NO_3S$	57·5	7·8	5·2
Dimethylamine [c]	99	129/0·01 mm.	67·4	8·45	4·1	$C_{11}H_{17}NO_2S$	67·25	8·5	4·35
s-Butylamine	97	146/0·07 mm.	61·3	8·6	5·7	$C_{13}H_{21}NO_2S$	61·1	8·3	5·5
Di-n-butylamine [d]	99	160/0·01 mm.	—	—	—	—	—	—	—

[a] M. p. [b] Reaction performed at 80°. [c] Reaction performed at −10° in ethanol. [d] Oxalate, m. p. 174—175° (lit.,* m. p. 173°).

* W. Reppe, *Annalen*, 1956, **601**, 111.

Kinetics.—Solutions containing appropriate concentrations of amine and sulphone, respectively, were allowed to attain the temperature of the thermostat (25·0°) during 30 min. The solutions were then mixed and aliquot parts (5 ml.) of the mixture were withdrawn at intervals. Two different analytical procedures were employed.

(a) *For reactive secondary amines.* The aliquot part was added to AnalaR carbon disulphide (3 ml.) in propan-2-ol (20 ml.). The dithiocarbamic acid formed was titrated against 0·05N-aqueous sodium hydroxide with phenolphthalein in pyridine as indicator. The method was tested for each amine (designated in Table 2) and the tertiary amine produced in the reaction was shown not to interfere with the determination. The method could not be applied to reactions for which t-butyl alcohol was the solvent.

(b) *For primary amines and weakly reactive secondary amines.* The aliquot part was added to an approximately four molar excess of thiophenol in oxygen-free ethanol. Thiophenol adds rapidly to the unchanged olefin in these conditions and the residual thiophenol was determined by

[34] D. L. Cottle, A. E. Jeltsch, T. H. Stoudt, and D. R. Walters, *J. Org. Chem.*, 1946, **11**, 286.

[35] L. I. Smith and H. R. Davis, *J. Org. Chem.*, 1950, **15**, 824.

Tamele and Ryland's method.[36] 0·1N-Sodium acetate (15 ml.) in oxygen-free ethanol was added and the thiophenol was titrated potentiometrically against silver nitrate in propan-2-ol. Titrations were performed with a Metrohm Combititrator 3D with silver and calomel electrodes.

A typical series of results is shown in Table 5.

TABLE 5

Rate of reaction of morpholine with p-tolyl vinyl sulphone in ethanol at 25°

Initial [amine] = 0·11. Initial [olefin] = 0·055

t (sec.)	180	345	465	573	720	960	1200	∞
0·05N-NaOH consumed (ml.)	8·50	7·45	7·00	6·70	6·40	6·10	5·90	5·70
10^2[Amine]	8·30	7·25	6·80	6·50	6·20	5·90	5·70	5·50

k from plot of $\log \frac{[\text{amine}]}{[\text{olefin}]}$ *vs.* t. = $3{\cdot}35 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$.

Additional runs: (i) [olefin] = 0·055M, [amine] = 0·0825M, $k = 3{\cdot}41 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$.

(ii) [olefin] = 0·055M, [amine] = 0·0275M, $k = 3{\cdot}39 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$.

Reversibility Tests.—(i) 2-Morpholinoethyl *p*-tolyl sulphone (134·5 mg.) was refluxed with piperidine (450 mg., 10 mol.) in ethanol (15 ml.) for 15 hr. Evaporation of the solvent gave recovered sulphone (99%), m. p. and mixed m. p. 64—66°.

(ii) 2-Morpholinoethyl *p*-tolyl sulphone (134·5 mg.), piperidine (225 mg., 5 mol.), and potassium t-butoxide (5·6 mg., 0·1 mol.) were stirred in t-butyl alcohol (10 ml.) for 24 hr. at 20°. The mixture was poured into water and extraction with ether gave recovered sulphone (60%), m. p. and mixed m. p. 63—64°.

TABLE 6

Orders of reaction of amines with *p*-tolyl vinyl sulphone in benzene at 25°

Amine	Initial [amine]	Initial [olefin]	10^4k_2 *	10^4k_3 †
Piperidine [method (*a*)]	0·075	0·05	128	2100
	0·1	0·05	185	3020
	0·15	0·05	265	2540
Morpholine [method (*a*)]	0·77	0·11	46·5	68·4
	0·33	0·11	19·9	77·8
	0·22	0·11	14·5	103
	0·165	0·11	12·0	106
	0·11	0·22	10·0	162
	0·11	0·33	10·2	187
Isopropylamine [method (*b*)]	0·15	0·10	0·39	3·00
	0·20	0·10	0·51	2·83
	0·30	0·10	0·76	3·66

* Apparent second-order rate constant in l. mole^{-1} sec.$^{-1}$.
† Third-order rate constant l.^{2} mole^{-2} sec.$^{-1}$.

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