

KINETICS OF THE CONDENSATION
OF 5-NITRO-2-FURFURYL DICHLOROMETHYL SULFONE
WITH ALDEHYDES*

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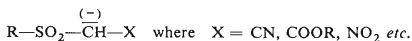
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The results are presented of kinetic measurements of the condensation reaction of 5-nitro-2-furfuryl dichloromethyl sulfone (*I*) with 5-X-2-furaldehydes *II* and 5-(X-phenyl)-2-furaldehydes *III*, where X = H, CH₃, Cl, Br, I, COOCH₃, NO₂, and Y = H, 4-CH₃, 4-Cl, 3,4-Cl, 4-Br, 4-COOC₂H₅, 2-NO₂, 3-NO₂, 4-NO₂. The effect of the substituent on the reactivity of the carbonyl component was investigated and the reactivity of sulfone *I* with other 5-nitrofurfuryl sulfones compared.

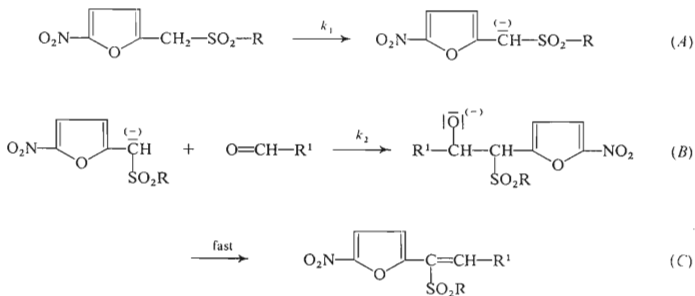
In preceding papers¹⁻⁴ we have described the preparation of saturated 5-nitrofurfuryl sulfones and investigated the kinetics of the condensation of some of them with aldehydes of furan and phenylfuran series. In connection with the study of the properties of 5-nitrofurfuryl sulfones it was found² that they are converted completely and rapidly to stable carbanions (equation (A)) under the effect of alkaline reagents, for example alcohates in alcohol, piperidine, *etc.* From this it follows that in this case the rate-determining step in the condensation reaction must be the addition of the carbanion formed on the carbonyl component, but not the cleavage of the C—H bond (ref.⁵⁻⁸). In comparison with the literature data⁶ we were unable to detect the formation of the intermediate (equation (B)) spectrophotometrically, from which it follows that the last step (equation (C)) is rapid (Scheme 1). In our case the bulkier and sterically more requiring carbanion (formed from *I*) undergoes condensation with the carbonyl group, similarly as in the case of "classical" sulfones in which the active methylene group is bound to the sulfone group and another electron-accepting group⁹:



Kinetic measurements of the reaction of sulfone *I* with aldehydes *II* and *III* were carried out by following the increase in the absorption of the K-band of the cor-

* Part LXXXII in the series Furan Derivatives; Part LXXXI: This Journal 42, 347 (1977).

responding α,β -unsaturated sulfone formed. On the basis of UV spectra of authentic unsaturated sulfones¹ the concentration increase of the product formed could be calculated from the extinction value, according to time. The results show that the reaction is a second order one. The advantage of the method used consisted in the possibility of carrying out the reaction, and thus also kinetic measurements, directly in thermostated cells. In order to increase the reliability of the kinetic measurements it was necessary to check whether in addition to condensation some other side reaction does not also take place, as for example the addition of methanol to the multiple bond of the unsaturated sulfone formed. For this purpose the behaviour of some α,β -unsaturated sulfones was also investigated, under the reaction conditions of the condensation reaction. The course of the possible addition was controlled on the basis of the UV spectrum change of the selected unsaturated sulfone. The measurements indicated that side reactions did not take place.



SCHEME 1

When comparing the values of rate constants of the condensation (Table I) of the two series – the furan and the phenylfuran one – it was evident that the aldehydes of the phenylfuran series enter the reaction with the corresponding saturated sulfone more willingly.

In both instances the logarithms of the rate constants were correlated with the σ_p -Hammett's constants of substituents (Fig. 1) and linear correlations were obtained with $\rho = 0.83$ and $r = 0.95$ for the furan series and $\rho = 0.48$ and $r = 0.90$ for the phenylfuran series. On the other hand, it is evident from Table II that the rate constant values also depend on the nature of the residue to the sulfo group, *i.e.* on the volume of the anion entering the reaction. The order of reactivity of individual carbanions is shown in Scheme 2.

TABLE I

Rate Constant Values k_2 and Half Times $t/2$ of the Reaction of 5-Nitrofurfuryl Dichloromethyl Sulfone with Aldehydes

Compound X or Y	$k_2 \cdot 10^2$ $l \text{ mol}^{-1} \text{ s}^{-1}$	$t/2 \cdot 10^{-4}$ s	σ_p
5-X-2-Furaldehydes			
H	12.40 ± 0.20	3.12	0
CH ₃	9.90 ± 0.04	4.05	-0.170
Cl	29.10 ± 0.04	1.37	+0.227
Br	26.84 ± 0.03	1.49	+0.232
I	33.35 ± 0.01	1.20	+0.276
COOCH ₃	30.85 ± 0.01	1.31	+0.385
NO ₂	36.29 ± 0.03	1.10	+0.778
5-(Y-Phenyl)-2-furaldehydes			
H	37.16 ± 0.05	1.08	0
4-CH ₃	27.50 ± 0.02	1.45	-0.170
4-Cl	29.98 ± 0.01	1.33	+0.227
3,4-Cl	41.21 ± 0.00	0.97	—
4-Br	48.50 ± 0.01	0.92	+0.232
4-COOC ₂ H ₅	66.74 ± 0.05	0.60	+0.450
2-NO ₂	99.70 ± 0.03	0.40	—
3-NO ₂	61.52 ± 0.02	0.62	+0.710
4-NO ₂	89.40 ± 0.05	0.47	+0.778

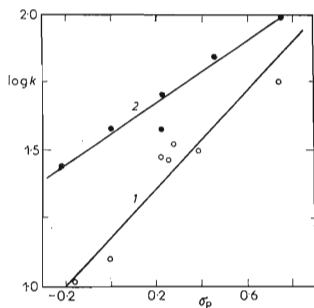
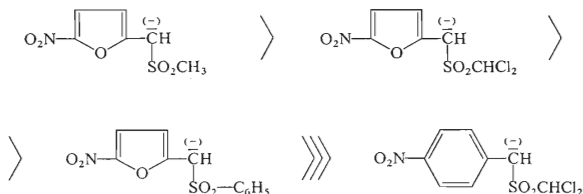


FIG. 1
Correlation of $\log k$ and σ_p of the Reaction of I with the Aldehydes of the Furan (1) and the Phenylfuran (2) Series

TABLE II

Rate Constants of the Condensation Reaction of Sulfones with 2-Furaldehyde (*A*), 5-Phenyl-2-furaldehyde (*B*) and 5-(4-Nitrophenyl)-2-furaldehyde (*C*)

R	$k_2 \cdot 10^2, \text{l mol}^{-1} \text{s}^{-1}$		
	<i>A</i>	<i>B</i>	<i>C</i>
—CH ₃	15.20 ± 0.10	40.82 ± 0.35	97.33 ± 0.50
—CHCl ₂	12.40 ± 0.20	37.16 ± 0.05	89.40 ± 0.25
—C ₆ H ₅	8.16 ± 0.05	15.60 ± 0.25	40.63 ± 0.50



SCHEME 2

In order to compare the reactivity of *I* with that of its benzene analogue, *i.e.* 4-nitrobenzyl dichloromethyl sulfone *IV*, kinetic measurements of the reaction of sulfone *IV* with 2-furaldehyde were carried out under the same conditions as in the case of compound *I*. This reaction did not take place at all. As found earlier¹⁰ sulfone *IV* condenses with some 5-substituted 2-furaldehydes only, while the yields of unsaturated sulfones do not exceed 10%. This fact indicates a substantially lower reactivity of *IV* in comparison with *I*, which is caused probably by the unwillingness of *IV* to be converted to the quinoid structure.

EXPERIMENTAL

A solution of 0.0001 mol of *I* in 200 ml of a 0.04M piperidine solution was prepared, with the final concentration of sulfone $c = 5 \cdot 10^{-4}$ M. At time $t = 0$ this solution was mixed at 41°C with a $5 \cdot 10^{-4}$ M solution of the corresponding aldehydes in methanol in a 1:1 ratio, and the starting concentrations of the sulfone, $c_0 = 2.5 \cdot 10^{-4}$ M, and of the aldehyde $c_0 = 2.5 \cdot 10^{-4}$ M, were thus obtained.

Kinetic measurements were carried out on a recording spectrophotometer Specord UV VIS Zeiss in the 200–450 nm region, in cells 1 cm thick, tempered at $41^\circ\text{C} \pm 0.2^\circ\text{C}$, at the wavelength of the absorption maximum of the K-band of the condensation product formed. In this region neither the sulfone nor the corresponding aldehyde show absorption bands.

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