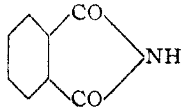
POLYSULFONES FROM VARIOUS CATALYSTS

Unsatd. compound	Amount, cc.	Catalyst to be tested	Amount in grams	Time, hr.	Yield of polysulfone, g.
1-Pentene	5	$NH_2OH \cdot HCl$	0.5	12	1.13
1-Pentene	5	$(CH_3)_3NO$	.5	12	4.5
1-Pentene	5		.5	12	3.5
1-Pentene	5	$(CH_3)_3NO$	.2	18	3.09
1-Pentene	5	$(CH_3)_3NO$	.2		
		HCl	2 cc., sp. gr. 1.19	18	5.17
1-Pentene	5	$C_6H_5(CH_3)_2NO$	5 cc., soln. in concd. HCl	12	1.0
1-Hexene	5	$(CH_3)_3NO$	0.2	12	6.15
		HCl	2 cc. dil.		
1-Heptene	5	$(CH_3)_3NO$	0.2	12	5.04
		HCl	2 cc., sp. gr. 1.19		
1-Pentyne	10	$(CH_3)_3NO$	0.5	18	13.38
2-Butene	10	$(CH_3)_3NO$	.5	18	16.00
2-Pentene	10	$(CH_3)_3NO$	.5	18	2.69
1-Heptene	5	$(CH_3)_4NCl$	.2	16	5.38
1-Pentene	5	$(CH_3)_4NCl$	.2	12	3.25
1-Pentene	5	$(C_2H_5)_4NBr$	.2	60	4.42
1-Pentene	5	$(n\text{-}C_7H_{15})(n\text{-}C_4H_9)_3NI$	.1	60	None
1-Heptene	5	$(n\text{-}C_7H_{15})(n\text{-}C_4H_9)_3NI$	.1	16	None

addition of halogen acid[2] to give the salt of the amine oxide increased the catalytic activity to a marked extent. Even hydroxylamine hydrochloride proved to have some activity as a catalyst for the reaction. More surprising was the fact that both tetramethylammonium chloride and tetraethylammonium bromide were catalysts for the reaction. Their activity, however, was not great. Tests with some quaternary ammonium iodides showed these were not catalysts for the addition reaction. Phthalimide also showed some catalytic activity.

Experimental

Trimethylamine oxide and dimethylaniline oxide were made by the method described by Hickinbottom.[3]

The polymerization reactions were carried out in pressure bottles. The unsaturated compounds and sulfur dioxide with a little ethyl alcohol were placed in the bottle with the substance to be tested as a catalyst. The sealed reaction mixture was allowed to stand for the specified time, then opened, the excess sulfur dioxide allowed to evaporate and the product isolated by the usual procedure. The results are summarized in the following table.

Trimethylamine oxide did not catalyze the addition of sulfur dioxide to vinyl chloride. Hydrazine, phenylhydrazine, cupferron, phenylglyoxal oxime, azoxybenzene, nitrobenzene, semicarbazide hydrochloride, dimethyl formamide, and hydrazocarbamide showed no catalytic activity at ordinary temperatures.

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[2] Kharasch and Sternfield [THIS JOURNAL, **62**, 2559 (1940)] have shown that the addition of hydrochloric acid increases the activity of the peroxide, ascaridole, as a catalyst for polysulfone formation.

[3] Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Company, New York, N. Y., 1938, p. 277.

Association Effects in the Raman Spectra of Solutions of Thiophenol in Donor Solvents

BY ROBERT H. SAUNDERS, M. J. MURRAY AND FORREST F. CLEVELAND

While the O–H stretching vibration gives strong absorption in the infrared and is quite suitable for use in the study of hydrogen bonding, the O–H frequencies in Raman spectra produce broad bands, so diffuse that in a great number of cases they are not even observed. On the other hand, the Raman spectra of mercaptans show a strong S–H line at 2570 cm.$^{-1}$ which is in a region not occupied by other fundamentals. For this reason it was hoped that a hydrogen bond study could be made of solutions of thiophenol such as Gordy and Stanford[1] had done in the infrared. Consequently, Raman spectra were obtained for pure thiophenol and for its solutions in benzene, dioxane, diisopropyl ether, pyridine, dibenzylamine and diisobutyl ketone. All compounds used were of good quality and were distilled before mixing. The apparatus and experimental technique used in obtaining the spectra are discussed

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[1] Gordy and Stanford, THIS JOURNAL, **62**, 497 (1940).

elsewhere.[2] Hg 4358 Å. was used for excitation, and the slit width of the spectrograph was 0.08 mm.

In order to determine whether mixing had altered disproportionately the intensity of the S–H line, the strength of the 2570 line was compared with that of the 700 cm.$^{-1}$ line of thiophenol on the same spectrogram. This latter line was chosen as a comparison line because it is neither too weak nor too strong for accurate intensity measurement, because it does not coincide with any lines of the various solvents employed, and because comparison of the intensity ratio of this line to lines other than 2570 cm.$^{-1}$ indicated no noticeable effect due to association. Semi-quantitative comparison was attained by use of a set of standard lines of regularly varied intensity.[3]

The results are listed in Table I. The number in parentheses following the Raman frequency represents intensity. The 700 cm.$^{-1}$ line which was used as a standard is arbitrarily given the value of 4 on each spectrogram. No attempt was made to compare the different spectrograms with each other. In general, the solutions employed were more dilute than those used by Gordy and Stanford. This was for the purpose of giving the mercaptan molecules as much chance to form hydrogen bonds as was experimentally feasible, since preliminary experiments indicated that the 50% by volume solutions did not show so large an effect as had been anticipated from the infrared data.

TABLE I

THE EFFECT OF DONOR SOLVENTS UPON THE S–H FREQUENCY OF THIOPHENOL

Solvent	Hours of exposure	Volume, % of thiophenol	S–H frequency Raman cm.$^{-1}$ I	S–H frequency Infrared[1] cm.$^{-1}$
Thiophenol (pure)	1	100	2569(7)	2577
Benzene	4	25	2571(7)	2577[a]
Diisobutyl ketone	4 and 11	25	2570(6)	..
Diisopropyl ether	4	25	2570(5)	2557[b]
Pyridine	4	50	2569(6)	2463[b]
Pyridine	4 and 9	25	2571(3)	2463[b]
Dioxane	4 and 8	25	2569(3) 2536(2)	..
Dibenzylamine	1	25	2571(6)[c]	2475[b]

[a] Dilute solution. [b] Fifty % by volume solution. [c] Solid separated from this solution at the end of one hour. Intensity reading somewhat in doubt.

As in the infrared work of Gordy and Stanford,[1] benzene was found to have negligible effect on the S–H frequency in the thiophenol–benzene solution. For mixtures of the mercaptan in diisobutyl ketone and diisopropyl ether the Raman line for the S–H stretching vibration is unchanged in frequency, somewhat broadened and only slightly decreased in intensity. For thiophenol-pyridine solutions the results are at complete variance with the infrared findings. In neither the 50% nor the 25% solutions is there Raman spectra evidence for an altered frequency. Furthermore, although in the 25% solution there is considerable decrease in the strength of the S–H line, it is evident that even in this more dilute solution the S–H groups of a sizable proportion of the thiophenol molecules are little affected by the presence of pyridine. The infrared results showed not only a shift of 114 cm.$^{-1}$ but also a large increase in absorptive power as compared to the pure mercaptan. The infrared showed no evidence for a band due to the unmodified S–H frequency in pyridine solution, but this may in part be caused by lack of resolution.

The Raman spectra results for the solution of thiophenol in dioxane are most striking. In this case the S–H frequency appears as a doublet composed of the original, unshifted, slightly broadened line and a new line (not observed in the spectra of either of the pure compounds) at 2536 cm.$^{-1}$ which is somewhat weaker and broad but clearly resolved from the 2569 cm.$^{-1}$ line. This is the only one of the compounds studied for which there is Raman spectra evidence of a modified frequency. In all the other cases tested in this investigation, if modified frequencies result they must be very weak or so broad and diffuse that they failed to register on the photographic emulsion in the time allotted.

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(2) Cleveland, Murray, Haney and Shackelford, *J. Chem. Phys.*, **8**, 153 (1940); Cleveland, Murray, Coley and Komarewsky, *ibid.*, **10**, 18 (1942).

(3) Cleveland and Murray, *ibid.*, **7**, 396 (1939).

Boiling Point–Composition Data of the Methyl Alcohol–Dioxane System

BY FRANK L. PADGITT,[1] EDWARD S. AMIS AND DAVID W. HUGHES[2]

In order to further extend the data of the methyl alcohol–dioxane system given by Amis,

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(1) Now employed by Ethyl Gasoline Corporation, Baton Rouge, La.

(2) Now employed by Tennessee Coal, Iron and Railway Company, Birmingham, Alabama.