Poly(carbamoyl Sulfonates) (Bisulfite Adducts of Polyisocyanates)

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Synopsis

In the reaction with aqueous sodium bisulfite of polyisocyanates derived from a poly(propylene oxide triol) (molecular weight 3000) and various diisocyanates, bisulfite adducts or poly(carbamoyl sulfonates) (PCS) are not formed unless a water-miscible lower alcohol or ether is used as solvent; and, with aromatic isocyanates, unless additional sulfite and/or a tertiary amine is added. The influence of reaction conditions on the yield of PCS has been examined in detail for the polyisocyanates derived from hexamethylene diisocyanate and 2,4-tolylene diisocyanate. PCS are water soluble, stable in acid solution, and hydrolyze in alkaline solution or on heating to insoluble polyureas. The chemistry of the reactions of PCS is reviewed and potential applications discussed.
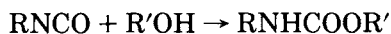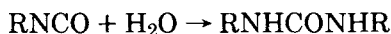
INTRODUCTION

When Petersen[1] described in 1949 the formation and reactions of isocyanate bisulfite adducts (carbamoyl sulfonates),
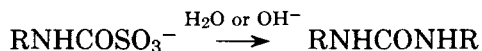Preparation:

$$RNCO + NaHSO_3 \rightarrow RNHCOSO_3^- \; Na^+ \qquad (i)$$

Side reactions:

$$RNCO + H_2O \rightarrow RNHCONHR$$

$$RNCO + R'OH \rightarrow RNHCOOR'$$

Reactions of carbamoyl sulfonates:

$$RNHCOSO_3^- \xrightarrow{\;H_2O \text{ or } OH^-\;} RNHCONHR$$

$$RNHCOSO_3^- + R'NH_2 \rightarrow RNHCONHR'$$

he noted that they could be of use in textile finishing, particularly bifunctional products, as these would form high molecular weight condensation products on the fibers as a result of an initial aqueous treatment. Since then, only occasional reference[2,3] to carbamoyl sulfonates, mainly from low molecular weight mono- and diisocyanates, has been made. Even though polyisocyanates are widely used, the lack of methods to prepare PCS in high yields has prevented their exploita-

tion. Work at CSIRO[4-8] has overcome this problem and resulted in the development of a new shrink-resist treatment for wool using PCS—the Sirolan BAP process.[8] Bayer AG· is now manufacturing a PCS for this application.

As part of the development of the Sirolan BAP process, the preparation and properties of PCS with various structures have been investigated in detail. This paper summarizes work on the bisulfite adducts (designated Ia ... etc.) of poly(ether polyisocyanates) I–XI prepared from a poly(propylene oxide triol) (molecular weight 3000, based on trimethylolpropane) and diisocyanates. Attention has been focused on the polyisocyanates I and II derived from hexamethylene diisocyanate and 2,4-tolylene diisocyanate, respectively, as these are typical aliphatic and aromatic diisocyanates and are similar to polyisocyanates used in surface coatings and cast elastomers. Shrink-resisting wool with PCS Ia–Xa has been reported briefly.[9] Work on other types of PCS will be reported later.

EXPERIMENTAL AND RESULTS

Commercial sodium metabisulfite of 95%–97% purity was used. These methods for the preparation of PCS are covered by CSIRO patent applications.

Preparation of Polyisocyanates

The polyisocyanates were prepared by heating dried Desmophen 3400 (Bayer), poly(propylene oxide triol), molecular weight 3000, and 5%–10% excess diisocyanate without solvent or catalysts for about 4 hr at the temperatures shown in Table I. The isocyanate content was determined by reaction with excess di-n-butylamine in dioxan and titration of the unreacted amine with hydrochloric acid.

TABLE I
Preparation of Polyisocyanates

Polyiso-cyanate[f]	Diisocyanate	Reaction temp., °C	Isocyanate content, %
I	Hexamethylene diisocyanate	110	3.5
II	2,4-Tolylene diisocyanate	60	4.1
III	Desmodur T65 (Bayer)[a]	60	4.2
IV	Desmodur T80 (Bayer)[a]	60	3.9
V	Isophorone diisocyanate (Veba)[b]	100	4.2
VI	Xylylene diisocyanate (Takeda)[c]	90	3.5
VII	Hylene W (du Pont)[d]	120	3.5
VIII	Trimethylhexamethylene diisocyanate (Veba)[e]	100	4.1
IX	2-Methoxycarbonylpentamethylene diisocyanate (Toray)	100	3.5
X	Bis(4-isocyanato-3-methylcyclohexyl)methane diisocyanate (BASF)	110	3.7
XI	4,4'-Diisocyanatodiphenylmethane	80	3.5

[a] 2,4- and 2,6-Tolylene diisocyanates, T65 = (65/35), T80 = (80/20).
[b] 3-Isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate.
[c] 70%-m and 30%-o.
[d] Bis(4-isocyanatocyclohexyl)methane.
[e] 2,2,4- and 2,4,4-Isomers.
[f] The corresponding PCS preparations have been numbered Ia ... etc.

Analysis of Carbamoyl Sulfonates

A PCS sample (5 g) was dissolved in a mixture of water (60 ml) and isopropanol (100 ml). Titration against 0.05M iodine solution containing potassium iodide to the iodine-color endpoint gives the free bisulfite content. Sodium hydroxide solution (10 ml of 300 g/l.) was then added to the titration solution and mixed thoroughly. After 2 min, this solution was acidified with sulfuric acid (25 ml of 200 g/l.) and immediately titrated against iodine. Sodium hydroxide quantitatively decomposes carbamoyl sulfonates to sulfite, which is estimated in the second titre. Control experiments established that aerial oxidation of sulfite was negligible under these conditions.

Reaction of Polyisocyanate I with Sodium Bisulfite

Influence of Solvent. To investigate this, a mixture of polyisocyanate I (4 g) and ethyl acetate (1 g) was dissolved in the solvent (45 ml), and a solution of sodium metabisulfite (0.35 g) in water (5 ml) was added with stirring.

After 24 hr, complete or partial gelation occurred with the following: water, acetone, methyl ethyl ketone, dimethylformamide, tetrahydrofuran, acetonitrile, formamide, sulfolane, butan-1,3-diol, diethylene glycol monomethyl ether, and diethylene glycol.

With the following solvents, gelation did not occur but dilution with water gave an insoluble precipitate: formic acid, acetic acid, dimethyl sulfoxide, hexamethylphosphoramide, 1,2-propylene glycol, 4-methylpentan-2-ol, N-methylpyrollidone, butan-1,4-diol, benzyl alcohol, diethylene glycol monoethyl, diethyl, and monobutyl ethers, ethylene glycol, furfuryl alcohol, ethylene glycol monobutyl ether.

In dioxan, 1,2-dimethoxyethane, and diethylene glycol dimethyl ether, about 80% conversion to carbamoyl sulfonate was obtained; but if more concentrated

TABLE II
Influence of Solvent in the Preparation of Ia

Solvent	% Conversion of Isocyanates to Carbamoyl Sulfonates		
	A[a] (dilute)		B[a] (more concentrated) after 24 hr
	After 10 min	After 24 hr	
Methanol	23	73	85
Ethanol	89	91	91
n-Propanol	20	78	54
Isopropanol	10	81	73
t-Butanol	3	56	32[b]
2-Methoxyethanol	gel		gel
2-Ethoxyethanol	16	86	86
Tetrahydrofurfuryl alcohol	25	85	gel
Dioxan	gel		gel
1,2-Dimethoxyethane	gel		gel
Diethyleneglycol dimethyl ether	gel		gel

[a] See experimental section.

[b] Water insoluble.

reaction mixtures were used, either I or sodium bisulfite separated and the yield dropped considerably.

The most effective solvents were investigated further, and the results are shown in Table II. In these experiments, a solution of polyisocyanate I (8 g) in ethyl acetate (2 g) was dissolved in the solvent with stirring, and without delay an aqueous solution containing sodium metabisulfite (0.7 g) was added. In set A, solvent (30 ml) and water (10 ml) were used, and, in set B, solvent (15 ml) and water (5 ml). Additional experiments in more concentrated solutions are shown in Table III, and the effect of bisulfite concentration is shown in Table IV.

Influence of the Concentrations of Ethanol and Water. As ethanol was the most practical solvent, it was investigated in some detail. Table V shows the results of experiments in which a solution of polyisocyanate I (40 g) in ethyl acetate (10 g) was reacted with a solution of sodium metabisulfite (4 g) in water and absolute alcohol with vigorous stirring. After 24 hr, water was added to redissolve any precipitated salts and the carbamoyl sulfonate content and functionality determined.

Large-Scale Preparation of Ia. The following method has been used on numerous occasions for the preparation of large batches of Ia. In a beaker, a solution of polyisocyanate I (1.6 kg) in ethyl acetate (400 g) was stirred mechanically with a wide-bladed paddle. Industrial methylated spirits (3.2 liter 95% ethanol containing 2% methanol) was added, and, as soon as the polyisocyanate had dissolved, a solution of sodium metabisulfite (160 g commercial food grade) dissolved in water (800 ml) was added. The reaction mixture was initially cloudy but cleared after 5–10 min. After half an hour, the mixture was diluted with water to give a product containing about 30% solids by weight. Such solutions can be concentrated *in vacuo,* but above 60% solids they were extremely viscous. This preparation can be acidified for improved shelf life by slowly stirring in a mixture of 30% hydrogen peroxide (20 ml) in water (40 ml).

Functionality of Ia. Ia prepared as above from I (40 g) in various ethanol–water mixtures was made up to a total volume of 250 ml so that the solvent contained 60% ethanol by volume. The functionalities were determined at a

TABLE III
Influence of Solvent and Concentration in Preparation of Ia[a]

Solvent, by volume	Total solids content, % by weight	% Conversion of Isocyanates to Carbamoyl Sulfonates[b]
75% Ethanol	25	87
	30	85
	35	82
	40	82
	45	76
	50	gel
75% Isopropanol	25	72
	30	70
	35	gel
85% 2-Ethoxyethanol	40	79
	50	gel

[a] Reaction of 80% solution of I in ethyl acetate with 10% excess sodium bisulfite.
[b] Determined after 24 hr.

constant volume to allow for intramolecular reactions which cause the apparent functionality to be concentration dependent, decreasing with dilution. The functionality was determined (for details see ref. 10) from the extent of reaction at the gel point in solutions to which excess triethylamine was added.

PCS IIa

To determine (see Table VI) the effect of coreactants, polyisocyanate II (10 g) was dissolved in dry dioxan (2.5 g) and stirred vigorously. Isopropanol (25 g) was added, immediately followed by an aqueous solution (18 g) of the co-reactants. After 15 min, by which time formation of carbamoyl sulfonates was complete, a sample was removed and the carbamoyl sulfonate group content determined. The results of such experiments are shown in Table VI.

To determine the influence of solvent composition, the organic solvent was added to a well-stirred solution of the polyisocyanate (10 g) in dry dioxan (2.5 g), immediately followed by an aqueous solution containing the bisulfite and other reactants. The results are shown in Table VII.

Such preparations decomposed to water-insoluble material after two to three days unless stabilized by the addition of a mixture of concentrated hydrochloric acid and isopropanol (1:4 by volume) at the rate of 2–4 ml per 100 g PCS solution.

PCS IIIa–Xa

The polyisocyanates were handled as 80% (by weight) solutions in dry ethyl acetate or dioxan, as these solutions were much less viscous and gave better yields in PCS preparations due to more even mixing. These solutions were dissolved

TABLE IV
Influence of Bisulfite Concentration in the Preparation of Ia[a]

No. of equivalents of bisulfite per isocyanate group	% Conversion of isocyanates to carbamoyl sulfonates	Effect of dilution of reaction mixture with water[b]	Appearance of product
0.2	20	precipitate	gels after 24 hr
0.4	39	precipitate	gels after 24 hr
0.5	49	precipitate	gels after 24 hr
0.6	58	milky solution	gels after 24 hr
0.7	67	faintly cloudy solution	viscous gels after 3 months
0.8	76	clear solution	gels after 6 months
0.9	85	clear solution	stable
1.0	92	clear solution	stable
1.1	91	clear solution	stable
1.2	91	clear solution	stable
1.4	89	clear solution	stable
1.6	85	clear solution	stable
1.8	82	clear solution	stable

[a] Reaction of polyisocyanate I (40 g) in ethyl acetate (10 g) with a solution of the bisulfite in water (50 ml) in ethanol (150 ml).
[b] After 2 hr.

TABLE V
Preparation of Ia in Various Ethanol–Water Mixtures

Expt. no.	Volume[a] of ethanol and water	% Ethanol, by volume	Initial appearance of reaction mixture	Time for reaction mixture to become homogeneous	Reaction time[b]	% Conversion to carbamoyl sulfonates	Apparent functionality
1	100 ml	50	2 phases	gels			
2		55	2 phases	2 hr	3 hr	67	2.8
3		60	2 phases	45 min	50 min	89	
4		65	2 phases	10 min	13 min	90	2.8
5		70	2 phases	5 min	6 min	93	
6		75	homogeneous	—	3	90	2.8
7		80	homogeneous	—	4	91	
8		85	two phases	15	16	76	2.8
9		90	two phases	never	2 hr	62	
10	150 ml	60	two phases	14 min	15 min	89	2.9
11		70	two phases	4 min	5 min	93	2.9
12		80	homogeneous	—	2 min	91	2.9
13		90	two phases	never	90 min	67	2.8
14	200 ml	50	two phases	gels	—	—	
15		55	two phases	50 min	60 min	81	
16		60	two phases	13	13	94	2.8
17		65	two phases	4	5	93	
18		70	two phases	2	5	94	2.8
19		75	homogeneous	—	2	90	
20		80	homogeneous	—	2	91	2.9
21		85	homogeneous	—	2	78	
22		90	two phases	never	partially water soluble	44	

[a] Reaction with polyisocyanate I (40 g) in ethyl acetate (10 g).
[b] To give a clear solution when a sample is diluted with 10 parts water.

in the alcohol by vigorous mechanical stirring and without delay a solution of sodium metabisulfite (10%–20% excess of 95%) in water was added. To obtain maximum yields, efficient stirring was essential and it was necessary to experiment with various solids contents and alcohol–water proportions.

The reaction mixture should not be heated, although the heat of mixing of alcohol and water may cause a slight rise in temperature. The reaction mixture may not be clear initially, and once it has clarified it may become cloudy again due to separation of inorganic salts. This can be prevented by adding a little water when the reaction is complete.

To improve the shelf life of the preparations, sufficient 20% sulfuric acid, 10% hydrochloric, and/or 10% hydrogen peroxide were added to give an apparent pH of about 2–3. With hydrogen peroxide, this usually corresponds to the point at which the slight greenish coloration (due to dissolved sulfur dioxide) disappears. The addition of acid may cause some salts to separate, but this can be prevented by dilution with a little water.

TABLE VI
Influence of Reaction Condition on the Preparation of PCS—IIa

Expt. no.	No. of moles of reactant per mole of isocyanate groups	% Conversion of isocyanate groups to carbamoyl sulfonates
1	1.2 $NaHSO_3$	14
2	1.5 $NaHSO_3$	17
3	1.2 $KHSO_3$	13
4	1.2 $NaHSO_3$ + 0.1 triethylamine	68
5	1.2 $NaHSO_3$ + 0.2 triethylamine	74
6	1.2 $NaHSO_3$ + 0.4 triethylamine	75
7	1.2 $NlaHSO_3$ + 0.6 triethylamine	73
8	1.4 $NaHSO_3$ + 0.1 triethylamine	66
9	1.4 $NaHSO_3$ + 0.2 triethylamine	73
10	1.4 $NaHSO_3$ + 0.4 triethylamine	80
11	1.0 $NaHSO_3$ + 0.2 triethylamine	72
12	1.0 $NaHSO_3$ + 0.1 Na_2SO_3 + 0.1 triethylamine	74
13	1.2 $NaHSO_3$ + 0.1 Na_2SO_3 + 0.1 triethylamine	71
14	1.2 $KHSO_3$ + 0.2 triethylamine	72
15	1.2 $NaHSO_3$ + 0.2 pyridine	17
16	1.2 $NaHSO_2$ + 0.2 2-methylpyridine	33
17	1.2 $NaHSO_3$ + 0.2 2,4,6-trimethylpyridine	64
18	1.2 $NaHSO_3$ + 0.2 N,N-dimethylaniline	10
19	1.2 $NaHSO_3$ + 0.2 tri-n-butylamine	75
20	1.2 $NaHSO_3$ + 0.2 triethanolamine	73
21	1.2 $NaHSO_3$ + 0.1 1,4-diazabicyclo-2,2,2-octane	73
22	1.2 $NaHSO_3$ + 0.5 dibutyltin dilaurate	17
23	1.0 $NaHSO_3$ + 0.2 Na_2SO_3	72
24	1.0 $NaHSO_3$ + 0.4 Na_2SO_3	74
25	1.0 $NaHSO_3$ + 0.6 Na_2SO_3	73
26	0.8 $NaHSO_3$ + 0.4 Na_2SO_3	82
27	0.6 $NaHSO_3$ + 0.6 Na_2SO_3	60
28	1.2 NH_4HSO_3	21
29	1.2 NH_4HSO_3 + 0.2 triethylamine	36
30	1.2 NH_4HSO_3 + 0.2 Na_2SO_3	49
31	0.6 $NaHSO_4$ + 0.6 $(NH_4)_2SO_3$	40

DISCUSSION

Preparation of the Bisulfite Adduct of Polyisocyanate I

Low molecular weight isocyanates form carbamoyl sulfonates in reasonable yield with aqueous bisulfite solutions,[1,6] but under these conditions the water-insoluble I hydrolyzes to useless polyurea. Stirring or emulsification only increases the rate of formation of polyurea, but if the reactants are brought together in the same phase by adding water-miscible organic solvents,[6–8] Ia may form. Homogeneous reaction mixtures containing I and sodium bisulfite were obtained

TABLE VII

Influence of Solvent Composition and Solids Content on the Preparation of PCS IIa

Expt. no.	Solvent, % composition by weight	Solids content, %	% Conversion of isocyanates to carbamoyl sulfonates	
			A. 1.2 NaHSO$_3$ + 0.2 triethylamine	B. 1.0 NaHSO$_3$ + 0.2 Na$_2$SO$_3$
1	60% Isopropanol	5	72	75
2		10	78	75
3		15	79	74
4		20	74	72
5		30	55	56
6		35	42	
7	40% Isopropanol	25	24	
8	50% Isopropanol	25	61	53
9	55% Isopropanol	25	66	64
10	60% Isopropanol	25	69	66
11	65% Isopropanol	25	62	56
12	70% Isopropanol	25	46	33
13	80% Isopropanol	25	36	
14	50% Ethanol[a]	25	36	
15	60%	25	69	
16	70%	25	52	
17	80%	25	18	
18	60% Ethanol[a]	15	70	
19	60% Ethanol[a]	20	69	
20	60% Ethanol[a]	30	65	
21	60% Methylated spirits[b]	25	55	
22	60% Methanol	25	23	
23	60% n-Propanol	25	66	
24	60% sec-Butanol	25	18	
25	60% t-Butanol	25	49	
26	60% 2-Methoxyethanol	25	17	
27	60% 2-Ethoxyethanol	25	15	
28	60% Dioxan	25	24	
29	60% Dimethylformamide	25	9	
30	60% 1,2-Dimethoxyethan	25	17	
31	Tetrahydrofurfuryl alcohol	25	15	
32	Diethylene glycol diethyl ether	25	15	

[a] Absolute.
[b] 95% Ethanol, 5% methanol, may contain acidic impurities.

with a number of solvents, but Ia was only formed to any extent in certain ethers (but only in dilute solutions) or lower alcohols. Concentrated solutions of Ia could be prepared directly in alcohols, particularly ethanol (see Tables III and IV). The effectiveness of alcohols was surprising in view of the ease with which alcohols and isocyanates react,[12] but the relative rates of reaction of butyl isocyanate with water, ethanol, and bisulfite were found[6] to be approximately 1:1.5:500,000. Amines react[12] much faster with isocyanates than alcohols, and alcohols have been used as solvent for amine–isocyanate reactions.[13,14]

The direct preparation of concentrated solutions of Ia using alcohols is, no doubt, aided by the formation of supersaturated solutions when alcohols are added to aqueous sodium bisulfite. This was most pronounced with ethanol and 2-ethoxyethanol, and it often took many hours for the sodium bisulfite to precipitate completely. Supersaturation did not occur with other water-miscible solvents or with potassium or ammonium bisulfites, or with other sodium salts, e.g., sulfite, sulfate, bisulfate, thiosulfate, or chloride. Potassium or ammonium bisulfite react with I, but it was not possible to prepare very concentrated PCS solutions with these reagents.[11]

In the preparation of Ia in different alcohols (Table II and III), there was wide variations in both the rate of reaction and the extent of formation of carbamoyl sulfonates. Ethanol was the most practical, giving the fastest reaction and highest yields, particularly in concentrated reaction mixtures. The reaction was much slower in isopropanol, and the yield was lower even though side reactions should be less, as secondary alcohols are less reactive toward isocyanates.[12] It was not necessary to use purified ethanol; and in large-scale preparations, industrial methylated spirits was satisfactory.[11]

There was an optimum range of ethanol–water proportions for maximum conversion of isocyanates to carbamoyl sulfonates. As the solids content increased, the range of optimum solvent compositions became smaller and the extent of conversion to carbamoyl sulfonates fell (see Tables II, III, and V). Even though the proportion of ethanol influenced the reaction time considerably, the effect on the final yield was much less marked.

The addition of tertiary amines or organometallic catalysts did not improve the yield of Ia; instead, side reactions of the isocyanates with water or alcohol were promoted. These side reactions, which inevitably occurred to a small extent with the trifunctional I, will affect the functionality of Ia; reaction with water

TABLE VIII
Shelf Life of Ia at Elevated Temperatures

Preparation	Shelf life,[c] days	
	60°C	70°C
30% Ia[a]	15 (30[d])	6 (10[d])
30% Ia + 0.2% H_2SO_4	~70 (80[d])	30 (40[d])
30% Ia + 0.4% H_2SO_4	~100	50
30% Ia + hydrogen peroxide[b]	~80	30

[a] Large-scale preparation, experimental section.
[b] See experimental section.
[c] Gel time or time to become water insoluble.
[d] Diluted with water 1:1.

TABLE IX
Preparation of PCS IIIa–Xa

No.	Coreactants[a]	Diluent[b]	Solvent, by volume	Solids content	% Conversion of isocyanates to carbamoyl sulfonates		
					After 10 min	After 20 min	After 24 hr
IIIa	1.2 NaHSO$_3$ + 0.2 Et$_3$N	dioxan	70% isopropanol	20	77	76	51 (75)[c]
IVa	1.2 NaHSO$_3$ + 0.2 Et$_3$N	dioxan	70% isopropanol	20	75	74	55 (74)[c]
Va	1.1 NaHSO$_3$	ethyl acetate	75% ethanol	20	64	82	90
VIa	1.1 NaHSO$_3$	ethyl acetate	75% ethanol	20	94	94	88
VIIa	1.2 NaHSO$_3$	ethyl acetate	80% ethanol	15	5	8	80
VIIIa	1.1 NaHSO$_3$	ethyl acetate	75% ethanol	20	87	92	95
IXa	1.1 NaHSO$_3$	ethyl acetate	75% ethanol	20	88	88	86
Xa	1.1 NaHSO$_3$	ethyl acetate	75% ethanol	20	10	19	95

[a] Number of equivalents per isocyanate.
[b] 25 g per 100 g Poly.
[c] Acid stabilized after 20 min.

increases the functionality of the product, whereas reaction with ethanol should cause a decrease. A detailed study[10] of the functionality of the PCS prepared from I under one set of reaction conditions showed a small increase in functionality (to 3.8 with a polyisocyanate I of functionality 3.2). However, in experiments (Table V) at different ethanol–water proportions, there were no significant differences in the apparent functionality.

Reaction of I with less than one equivalent of bisulfite per isocyanate group (see Table IV) resulted in rapid gelation below about 0.5 equivalent; and below about 0.8 equivalent, the products were viscous and gelled after several months. With a large excess of sodium bisulfite, the carbamoyl sulfonate formation dropped; this may be due to a reduction in the free sulfite concentration, the species which actually reacts with the isocyanates.[6]

Stability of PCS Ia

Thirty percent solutions of Ia after two years of storage at 20°C still contained 85% or more of the carbamoyl sulfonate originally present, but preparations containing more than 40% solids or those in which there had been less than 85% initial conversion of isocyanates to carbamoyl sulfonates had poorer shelf life.[11] The shelf life of PCS could be improved (see Table VIII) by adding hydrochloric or sulfuric acid but not acetic or formic acid,[11,15] by adding hydrogen peroxide (which forms sulfuric acid by oxidizing the residual bisulfite),[15] by adding organic sulfonic acids[16] or, to a lesser extent, by dilution.[11]

This "acid stabilization" is due to the rate of hydrolysis of carbamoyl sulfonate falling as the pH decreases.[6] PCS preparations are probably to some extent self-stabilizing as aerial oxidation of residual bisulfite or any bisulfite released on hydrolysis caused the preparations to become more acidic. For an explanation for the dependence of the shelf life on concentration and the initial yield of carbamoyl sulfonates, consider the extent of reaction, p, at the gel point of a PCS of functionality f which is given by eq. (ii):[10]

$$p = (f - 1)^{-1} \qquad \text{(ii)}$$

Therefore, increasing the apparent functionality decreases p and reduces the gel time, which will be reflected in reduced shelf life. In gel point experiments, the apparent functionality obtained increases with concentration as intramolecular reactions become less favorable.[10] Preparations of Ia with low conversions to carbamoyl sulfonates were more viscous, suggesting increased molecular weight from side reactions of isocyanates with water; and as it is polyfunctional, the functionality should have been increased.

Bisulfite Adduct of Polyisocyanate II

The optimum methods to convert I into Ia gave low conversions with II, forming useless products;[8] but reasonable yields of IIa could be obtained by adding sodium sulfite and/or tertiary amines[17] to the reaction mixture (see Table VI); however, the maximum extent of conversion to IIa was still less than with Ia. The optimum ethanol concentration to prepare IIa was lower and the range of usable compositions narrower, and the yield dropped more rapidly with increasing solids content, when compared with the preparation of Ia (see Table

VII). In contrast to Ia slightly higher yields of IIa were obtained in isopropanol than ethanol.

Tertiary amines catalyze reactions of isocyanates with alcohols,[12] although in this case they probably only increase the sulfite concentration by neutralizing bisulfite. The yield of IIa increases with the tertiary amine base strength, and pyridine which catalyzes some isocyanate reactions[12] was not effective. The effect of adding sulfite or tertiary amine can, therefore, be accounted for by the mechanism proposed[6] for the butyl isocyanate–bisulfite reaction where it was demonstrated that the species which actually reacts with the isocyanate is sulfite, not bisulfite. A similar mechanism has been advanced for the addition of bisulfite to aldehydes and ketones.[18]

Even though aromatic isocyanates are more reactive than aliphatic ones—I and II gel in 60% ethanol in 3 hr and 15 min, respectively, at 20°C[11]—the reaction with sulfite should also be faster, which suggests a smaller rate difference between the reaction of aromatic isocyanates with bisulfite and water or alcohol compared with aliphatic isocyanates.

PCS IIa hydrolyzed much faster than Ia and, unless acidified immediately after the reaction, decomposed to useless material within several days. In acid solutions, IIa was stable and had a shelf life of over a year.[11]

Bisulfite Adducts of Polyisocyanates III–XI

Experiments on the formation of PCS from polyisocyanates III–XI are summarized in Table IX. Gelation occurred with the polyisocyanate XI; and with the slow-reacting VII, lower conversion was obtained presumably due to separation of bisulfite from the supersaturated reaction mixture.

PCS preparations have also been prepared[11] from other polyisocyanates derived from poly(propylene oxide) polyols with lower molecular weights and functionalities and a number of commercial poly(ether polyisocyanates) of undisclosed structures. Polyisocyanates used for surface coatings often contain solvents which should be removed in order to obtain good conversions to carbamoyl sulfonates. In general, as the isocyanate content of the polyisocyanate increased, the conversion to carbamoyl sulfonates decreased, probably because of the problem of keeping increasing amounts of bisulfite in solution.

Properties and Reactions of PCS

The PCS Ia–Xa are readily soluble in water giving solutions with low surface tensions. The carbamoyl sulfonate group is an effective solubilizing group for the poly(propylene oxide) backbone, although the polar nature of such polyethers no doubt assists. Poly(propylene oxide) PCS preparations of this type with equivalent weights 1500–2000 are readily water soluble, whereas the parent polyols are not.[11]

Carbamoyl sulfonates have different reactivity from the parent isocyanates, which has useful technical consequences. The preparation and storage of PCS in aqueous media depends on the rate of hydrolysis at room temperature of carbamoyl sulfonates being less than isocyanates, otherwise conversion of a polyisocyanate into a water-soluble form would only serve to facilitate hydrolysis.

At higher temperatures, the rate difference in hydrolysis of PCS and polyisocyanates appears to be smaller; for example, Ia and I cure on wool at similar

rates at 100°C, but at 20°C, Ia cures very much more slower.[9] This is probably a reflection of the differences in the activation energies, 87 ± 5 and 62.3 kJ/mole, reported for the hydrolyses of butyl carbamoyl sulfonate[6] and butyl isocyanate,[19] respectively.

A further consequence of the reduced reactivity of carbamoyl sulfonates is that, apart from hydrolysis to symmetric ureas, the only other reactions reported[1,6] are with primary and secondary amines to form unsymmetric ureas, reactions (i). Reactions of carbamoyl sulfonates with weaker nucleophiles are not observed, presumably because hydrolysis by the water inevitably present forms more reactive amines.
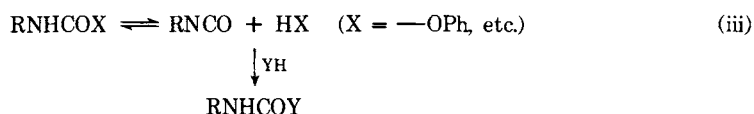
Mechanism of Carbamoyl Sulfonate Hydrolysis

The hydrolysis of PCS to polyurea will be considered in detail as this reaction is the basis of PCS shrink-resist treatments.[4–8] In many discussions of isocyanate chemistry, carbamoyl sulfonates have been classified as "blocked isocyanates" which decompose thermally to reform free isocyanate, reaction (iii):[12,20]
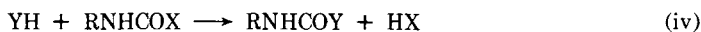
Mechanisms of Carbamoyl Sulfonate Reactions
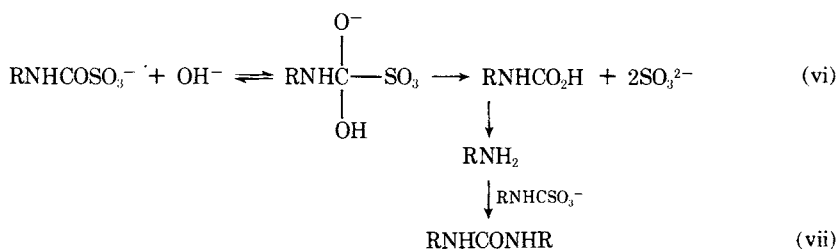
Blocked Isocyanates

Unblocking:

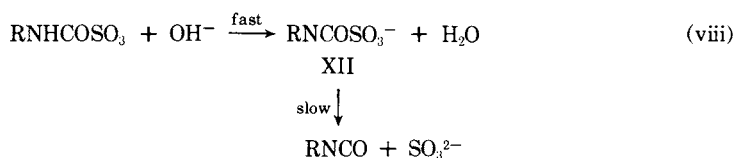$$RNHCOX \;\rightleftharpoons\; RNCO + HX \quad (X = -OPh, \text{ etc.}) \tag{iii}$$

$$\downarrow YH$$

$$RNHCOY$$

Direct substitution:

$$YH + RNHCOX \longrightarrow RNHCOY + HX \tag{iv}$$

"Unblocking" or S_n1 Mechanism

$$RNHCOSO_3^- \;\overset{\Delta}{\rightleftharpoons}\; RNCO + HSO_3^- \tag{v}$$

S_n2 ($B_{ac}2$) Mechanism

$$RNHCOSO_3^- + OH^- \;\rightleftharpoons\; RNH\overset{\displaystyle O^-}{\underset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}\!\!-SO_3 \longrightarrow RNHCO_2H + 2SO_3^{2-} \tag{vi}$$

$$\downarrow$$

$$RNH_2$$

$$\downarrow RNHCSO_3^-$$

$$RNHCONHR \tag{vii}$$

El_cB Mechanism

$$RNHCOSO_3 + OH^- \overset{fast}{\longrightarrow} RNCOSO_3^- + H_2O \tag{viii}$$

$$XII$$

$$\text{slow} \downarrow$$

$$RNCO + SO_3^{2-}$$

Mechanism of Carbamoyl Sulfonate Formation

$$RNCO + SO_3^{2-} \overset{slow}{\longrightarrow} RNCOSO_3^- \overset{fast}{\longrightarrow} RNHCOSO_3^- \tag{ix}$$

$$XII$$
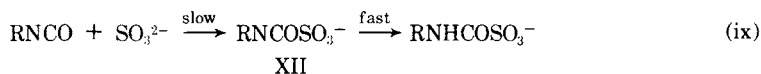
This type of thermal equilibrium, reaction (v), has been considered[6,21] for PCS. However, it is generally[20] appreciated that other reaction pathways, e.g., the direct substitution, reaction (iv), are significant with blocked isocyanates, and this also seems to be the case with PCS.

The strongest evidence against the equilibrium (v) is that PCS preparations are stable in neutral and acid aqueous solutions at room temperature,[6,11] whereas the corresponding isocyanates rapidly hydrolyze and the rate of hydrolysis is higher in acid solution than in neutral solution.[22] For example, I in aqueous dioxan gels in a few hours at 20°C and hydrolyzes very rapidly if acid is added, whereas in acid solution Ia is stable for at least four years. Also, PCS are stable in the presence of oxidizing agents or barium salts which would be expected to remove bisulfite and shift the equilibrium to the right.[6,11] Thus, if there is an equilibrium, the equilibrium constant must be extremely small at 20°C, and it is difficult to see why this should change significantly at 100°C as required by the S_n1 mechanism, reaction (v).

The thermal decomposition of the potassium bisulfite adduct of butyl isocyanate[6] was investigated (Table X) by heating under a vacuum of 0.5 mm/Hg. Butyl isocyanate (boiling point 115°/760 mm), if formed, should be removed; however, there was only slight loss in carbamoyl sulfonate content after several hours at 100°C. In contrast, Ia cures on wool in a few minutes at 100° in steam;[9] therefore, hydrolytic reactions must be involved rather than the thermal equilibrium (v). This would explain the observation[7] that for the development of shrink resistance with a PCS, it was necessary to have water present as well as heat.

The rate of hydrolysis of n-butylcarbamoyl sulfonate increased continually as the solution became more alkaline, and there was no apparent leveling off or increase in rate in acid.[6,11] In the pH range of 2–7, plots of log K (at 60°–80°C) against pH gave[6] straight lines with slopes of about $1/2$, and studies[11] in the range of 7–11 (at 20°) have found a similar linear relationship. Above pH 11, the rate was extremely fast. The observed pH dependence suggests base catalysis or direct reaction with hydroxide ion and is not consistent with an S_n1 mechanism, such as the forward reaction of the equilibrium (v) which should be independent of pH, although the reverse and subsequent reactions may not be. The most likely mechanism is the S_n2 or $B_{ac}2$ reaction (vi), but it is also necessary to consider the base-catalyzed $E1_cB$ reaction (viii) to account for the detection[6]

TABLE X
Thermal Decomposition of Potassium Butylcarbamoyl Sulfonate[a]

Heating conditions	Carbamoyl sulfonate groups remaining,[b] %
1.0 hr 100°C	97
2.0 hr 100°C	96
0.5 hr 120°C	95
1.0 hr 120°C	81
2.0 hr 120°C	67
1.0 hr 140°C	8

[a] Heating in glass under 0.5 mm Hg.
[b] Determined iodometrically.

by infrared spectroscopy of some isocyanate intermediate in the hydrolysis of n-butylcarbamoyl sulfonate at pH 6 and 80°C. In the $E1_cB$ mechanism, the loss of a proton to form the dianion XII should be rapid and thus not rate determining; however, as the amide-like NH proton will only be weakly acidic, the concentration of XII should depend on the pH. Thus, the rate of the $E1_cB$ reaction would be expected to increase with pH until, in very strong alkali, it levels off to a constant value.

Support for the $E1_cB$ mechanism comes from the hydrolysis of carbamate esters ($RNHCO_2R'$) where this type of mechanism with isocyanate intermediates has been established[24,25] and with carbamoyl phosphates ($RNHCOPO_4^{2-}$) where it is also considered to occur.[24] With carbamate esters, the $E1_cB$ mechanism, if possible, is much more favorable than the $B_{ac}2$ reaction, as some disubstituted esters (R_2NCO_2R') hydrolyze up to 10^6 times slower than monosubstituted analogues ($RNHCO_2R'$).[24,25] The $E1_cB$ reaction (viii) is, in effect, the reverse of the mechanism, equation (ix), established[6] for the formation of carbamoyl sulfonates, i.e., a rate-determining addition of sulfite (not bisulfite) to the isocyanate, followed by rapid protonation. Aldehyde and ketone bisulfite adducts hydrolyze by an $E1_cB$ mechanism, also the reverse of the mechanism of their formation.[18]

Williams[24] has discussed the use of entropy of activation to distinguish between $E1_cB$ and $B_{ac}2$ mechanisms in carbamate hydrolysis, but it is not unequivocable; $B_{ac}2$ mechanisms usually give larger negative values than $E1_cB$ mechanisms. An S_n1 mechanism, reaction (v), would be expected to show a positive entropy of activation (e.g., as found[25] for the hydrolysis of diphenyl carbamoyl chloride). Calculations[11] from the limited amount of kinetic data[6] at different temperatures for the hydrolysis of butyl carbamoyl sulfonate suggest a large negative value (approx. -20 eu) for the entropy of activation.

With the $E1_cB$ mechanism, even if it was the major reaction pathway, there will only be a very small steady-state concentration of free isocyanates as their subsequent reactions with water or amines are faster. Furthermore, if the $E1_cB$ mechanism was the sole pathway, not every carbamoyl sulfonate would be converted to an isocyanate, as many will react in an S_n2 reaction with the amines formed, reaction (vii). In PCS containing several carbamoyl sulfonate groups which react independently, as in Ia, the amount of the free parent polyisocyanate reformed throughout hydrolysis must be quite small. Thus, in understanding the textile applications of PCS, it would appear incorrect to consider that the PCS is converted back to the parent isocyanates which then behaves in the same way as if it were applied from a solvent.

Urea Formation in Carbamoyl Sulfonate Hydrolysis

The extent, as well as the rate, of urea formation from PCS hydrolysis is important as the ureas crosslink the cured polymer. Thus, factors such as pH, temperature, and solvent will influence properties of the cured polymer. For example, in polyisocyanate shrink-resist treatments for wool, the extent of urea crosslinking was found to influence the shrink-resist effectiveness,[28] and similar effects would be expected with PCS.

The conversion of carbamoyl sulfonate to symmetric urea will be prevented in strong acid or alkali. In acid solutions, the intermediate amine will be pro-
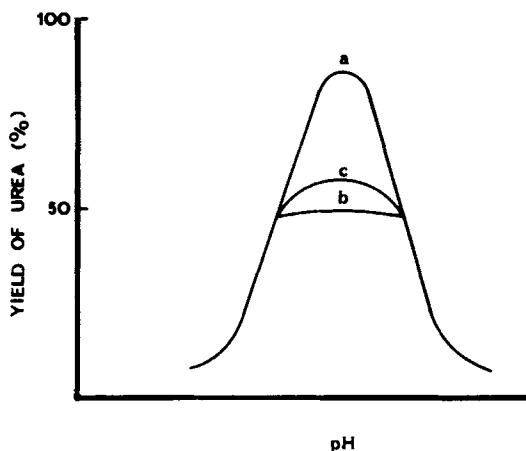
Fig. 1. Influence of pH on extent of urea formation in carbamoyl sulfonate hydrolysis: (a) hydrolysis of a monocarbamoyl sulfonate; (b) hydrolysis of a PCS at the gel point; (c) hydrolysis of a PCS at complete reaction.

tonated, which prevents subsequent reaction with either isocyanates or carbamoyl sulfonate to form ureas. In strong alkali, the intermediate carbamic acid salt accumulates, as the rate of hydrolysis of carbamate to amine shows the reverse pH dependence to carbamoyl sulfonate hydrolysis, i.e., decreased with increasing pH.[27] Thus, urea formation from a mono- or dicarbamoyl sulfonate would be expected to show a pH dependence, with the maximum yield of urea (which must be less than 100%) occurring in a narrow, slightly alkaline pH region as shown in Figure 1.

In the hydrolysis of a polyfunctional carbamoyl sulfonate, urea formation gives a product of increased molecular weight. If the functionality is greater than 2, a gel of infinite molecular weight forms, provided urea formation is not rate limiting, such as in strong acid or alkali. As discussed above, eq. (ii) gives the extent of reaction at the gel point which must be less than 1. Some additional ureas will form after the gel point, but this will be hindered by the restricted mobility of reacting groups in a gel and their wide separation in structures such as Ia. The overall effect of gelation in PCS hydrolysis (summarized in Fig. 1) is to make the extent of urea formation less pH dependent than with monocarbamoyl sulfonates.

Applications of PCS

PCS I–Xa can be used to shrink-resist wool.[4,9] This application utilizes the water solubility of PCS, the ready hydrolysis to an insoluble polyurea at 100°C together with stability of PCS in neutral or acid solutions at room temperature. This combination of properties may find other applications. Also, conversion to a water-soluble form overcomes two of the problems associated with handling polyisocyanates, namely, their sensitivity to reaction with moisture and the toxicity of any residual diisocyanate. A water-soluble product facilitates industrial application of textiles from established equipment designed for aqueous processing and avoids problems associated with organic solvents.

Such considerations suggest that PCS may also be useful for coating various

substrates in particular leather or paper. In considering potential applications, the following points should be noted:

(1) The curing of a PCS releases an inorganic salt.

(2) The bisulfite released during curing acidifies the reaction mixture which is increased by subsequent aerial oxidation of bisulfite. This acidification reduces the rate of hydrolysis of carbamoyl sulfonate and may inactivate polyamine crosslinking agents, if present, by protonation.

(3) The different reactivity of PCS to polyisocyanates influences the choice of crosslinking agents. Crosslinking with polyols is feasible only under anhydrous conditions. Polyamines that gel immediately on mixing with polyisocyanates may react at a more controllable rate with PCS.

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