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Esterification of phosphonocarboxylic acids and crosslinking of cellulose

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Summary — A number of phosphonocarboxylic acids, including those known to be good crosslinking reagents for cellulose, give a clear correlation between this property and the ability to be esterified by alcohols such as (tetrahydro-2-pyranyl)methanol and *trans*-1,2-cyclohexanediol at 180 °C. Phosphonic esterification takes place only in the presence of a β-COOH function and appears as a necessary condition for the crosslinking ability, provided that enough carboxylic esterification can take place. Cyclic five-membered anhydrides are proposed as reaction intermediates but only carboxylic anhydrides could be evidenced.

phosphonocarboxylic acid / phosphonic esterification / cellulose crosslinking

Résumé — Estérification d'acides phosphonocarboxyliques et réticulation de la cellulose. L'étude d'acides phosphonocarboxyliques, dont certains sont de très bons réticulants de la cellulose, a permis d'établir une corrélation entre cette caractéristique et la facilité de l'estérification par des alcools tels que le (tétrahydropyran-2-yl)méthanol et le *trans*-cyclohexane-1,2-diol à 180 °C. L'estérification de la fonction phosphonique n'a lieu qu'en présence d'une fonction COOH située en β et semble une condition nécessaire pour l'apparition du pouvoir réticulant, sous réserve d'une estérification des fonctions carboxyliques suffisante. Divers anhydrides cycliques à cinq chaînons sont proposés comme intermédiaires réactionnels mais seuls les anhydrides carboxyliques ont pu être mis en évidence.

acide phosphonocarboxylique / estérification phosphonique / réticulation de la cellulose

Cellulose crosslinking to provide durable wrinkle resistance to cotton fabrics has been an industrial challenge since artificial fibers appeared in textile industry. A number of reagents were investigated a long time ago and valuable processes are now in use to obtain unwrinkable cotton. However, all of them display one or several drawbacks: yellowing and reduced mechanical strength of fabrics; decreasing of wrinkle resistance through laundering operations; elevated cost; and, above all, release of toxic products during production, storage or use. The last point is responsible for the active search of new reagents to replace widely used efficient *N*-hydroxymethyl agents, which are susceptible to release formaldehyde vapor.

A large amount of research on polycarboxylic acids [1] has shown that when some of them are used with catalysts, they are very efficient as cellulose crosslinking reagents and are also non-yellowing. They also have very low toxicity and are resistant to numerous home washings owing to unreacted carboxylic functions. A question is the cost of the reagents, which are not industrially available.

More recently, it was found that phosphonocarboxylic acids, some of which are already used in other industrial fields, could be efficient in the treatment of cotton, without any of the drawbacks of *N*-hydroxymethyl agents [2]. Because the mechanism of crosslinking was unknown, we decided to study the reaction of alcohols, in the role of simple models of cellulose, with various phosphonocarboxylic acids, in order to determine relationships between the structure of the latter, their ability to react and their technical efficiency as cellulose crosslinking reagents.

Preliminary study: choice of reagents and analysis of reaction products

The complex fibrous structure of cellulose indicates that it does not simply react as a chemical compound containing a number of alcoholic functions, particularly in the crystal-like areas. However, in its so-called 'amorphous' areas, which are responsible for the wrinkling of cotton, cellulose is more or less penetrated by soluble reagents and, in the presence of acids, a number

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of hydroxylic functions should be able to be esterified. This is actually the case when pure cotton is reacted with polycarboxylic acids, as evidenced by IR analysis [3]. It can thus be supposed that cellulose crosslinking by phosphonocarboxylic acids is due to esterification of hydroxylic functions of cellulose by acidic sites of reagents.

Choice of alcohols and acids

Cellulose, a glucose polymer, can be seen as a series of units made of a primary alcohol and a secondary α-diol borne by a tetrahydropyranyl skeleton. As in a previous work on cellulose crosslinking by glyoxal [4], first (tetrahydro-2-pyranyl)methanol (referred to as 'Thol' in the following) then *trans*-1,2-cyclohexanediol were reacted, knowing that precise identification of all species would be a difficult task, particularly in the latter case.

Cellulose crosslinking cannot take place unless a single molecule of reagent can react with at least two hydroxylic functions belonging to two different cellulose fibers. The compared reactivity of the available alcoholic functions is obviously an important factor in the process of crosslinking.

The choice of acids came from technical results of crosslinking experiments [2] indicating that 2-phosphonosuccinic acid is a much more efficient reagent than 2-phosphonoglutaric acid, which is practically ineffective when no catalyst is used. In order to compare the reactivities and, above all, to have a chance to analyze all the esters formed in the process, we first studied two simple models of the above acids, ie, 2-phosphonoacetic and 3-phosphonopropanoic acids. In the following, the phosphonocarboxylic acids will be called C*n*m*m*P (fig 1), where n and m refer to the numbers of carbon atoms bearing a carboxylic function; the length of skeleton is given by the greatest figure, given that phosphonic function is borne by carbon atom C1.

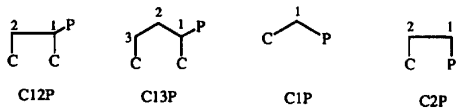

Fig 1. Simplified names and structures of four phosphonocarboxylic acids (C for COOH, P for PO_3H_2).

Analysis of species present in the reaction mixture

Preliminary experiments have shown that the number and the percentage of species observed in reaction mixtures varied largely with reagents and reaction conditions. Our best analytical tool was found to be ^{31}P NMR chemical shifts, which vary systematically with structures and could be directly measured in reaction mixtures.

With the help of ^{13}C and ^{1}H NMR spectra, we first identified a number of independently prepared simple esters and could establish structure/^{31}P chemical shift correlations, which then enabled us to study complex esterification mixtures, as previously reported [5]. For esters derived from a given phosphonocarboxylic acid and Thol, the degree of esterification of the phosphonic function was always unambiguously determined as was, in most cases, the degree of esterification of every carboxylic function present in the skeleton. Extended to esters obtained from *trans*-1,2-cyclohexanediol, these rules led to interesting but less precise results.

On the other hand, quantitative analysis of spectra gave the proportions of species present in the reaction mixtures. Results obtained in various reactions could be compared, with an uncertainty of about 10%, due to the rather poor quantitative reproducibility of ^{31}P NMR spectra.

Esterification of phosphonocarboxylic acids

In order to be able to apply our results to the cellulose problem, reagents were reacted in conditions similar to those used in industrial curing of cotton fabrics, ie, at 180 °C with an excess of alcohol, over a few minutes and in the presence of enough basic reagent (here NaH) to neutralize the first acidic phosphonic function. The presence of small quantities of water could not be avoided or precisely measured; a number of our experiments were run several times in order to minimize this factor.

For the sake of comparison and to indicate the trends, many reaction mixtures were analyzed after 2 and 5 min and also after 10, 15, 30, 60 min or longer and the same reagents were reacted in the same conditions but without a base. We also studied ethylphosphonic acid, which is known to be quite unable to crosslink cellulose.

The calculated rates of esterification of phosphonic (P%) and carboxylic function(s) (C%) for the five acids $EtPO_3H_2$, C1P, C2P, C12P and C13P (fig 1) are reported in table I. These rates are related to complete esterification of the function(s), taking into account an important precision about the phosphonic function: the figures are related to total *mono*phosphonate formation, because very low (if not zero) rates of diphosphonates were observed, whatever reagents and conditions. The remaining acid rates (Ac%) provide values of global esterification rates.

Esterification by Thol

• *Rates of esterification*

Table I shows that the ability of phosphonosuccinic acid (C12P) to be esterified is the best. This is most interesting because this acid is the best crosslinking reagent in the series studied. Phosphonic esterification of this acid is similar to C2P, while the phosphonic function is very poorly esterified in both C13P and C1P, as in the case of ethylphosphonic acid. The rates of phosphonic esterification for C2P and C12P are very different from the other acids. Carboxylic esterification, which is generally easier than phosphonic esterification, is easier for C12P and C1P than for C2P and C13P.

Some correlations between the ability to be esterified and the crosslinking efficiency of the acids are shown below.

Table I. Esterification of Thol[a].

Acid	*Reaction time (min)*						
	2	*5*		*15*	*30*	*50*	*60*	
	5 mol ROH[b]	*5 mol ROH*[b]	*10 mol ROH*[b]	*5 mol ROH*[b]	*5 mol ROH*[b]	*5 mol ROH*[b]	*5 mol ROH*[b]	*10 mol ROH*[b]
$EtPO_3H_2$								
P%			0 (2)		0 (4)			20 (30)
C%			–		–			–
Ac%			100 (98)		100 (96)			80 (70)
C1P[c]								
P%		0 (0)			4 (2)		– (8)	
C%		53 (90)			74 (97)		– (100)	
Ac%		47 (100)			26 (3)		– (0)	
C2P								
P%		24 (35)	51 (42)	63 (45)	61 (52)	– (59)	66 (72)	
C%		26 (84)	33 (82)	53 (95)	85 (96)	– (79)	73 (75)	
Ac%		61 (10)	25 (7)	14 (2)	3 (1)	– (5)	11 (5)	
C12P								
P%	– (15)	17 (20)	26 (38)	60 (37)	60 (34)	66 (40)	– (49[d])	
C%	– (27)	45 (49)	51 (50)	77 (88)	80 (78)	92 (86)	– (92)	
Ac%	– (38)	11 (17)	5 (7)	0 (0)	0 (2)	0 (0)	– (0)	
C13P[e]								
P%		4 (1)		0 (2)	24 (7)		38 (13)	
C%		32–37 (61)		53 (62–82)	67–79 (87–95)		64–87 (82–85)	
Ac%		40 (6)		19 (1)	2 (0)		0 (0)	

[a] Esterification rates of phosphonic (P%) and carboxylic (C%) acids, followed by rates of remaining acids (Ac%), from ^{31}P NMR spectra (experimental uncertainty $\geqslant$ 5%). Reaction temperature 180 °C, 1 mol of NaH for 1 mol of phosphonic acid (in parentheses results without a base). [b] 5 or 10 mol of Thol/total carboxylic and phosphonic functions (Z-PO_3H_2 = one function). [c] After 15 h, P% = 54%, C% = 97%, Ac% = 0. [d] Mean value (variations from 39 to 59%). [e] Lack of identification of phosphonates, precise values not known.

Global esterification rates:

$$C12P >> C13P, C1P > C2P >>> EtPO_3H_2$$

Phosphonic esterification rates:

$$C2P > C12P >>> C13P > C1P > EtPO_3H_2$$

Carboxylic esterification rates:

$$C1P, C12P >> C13P, C2P$$

The experimental classification as crosslinking reagents [2] is

$$C12P > C2P >>> C13P > C1P > EtPO_3H_2$$

(actually the last two acids are ineffective).

The ability of the phosphonic function to be esterified is clearly a necessary condition for crosslinking efficiency. On the other hand, crosslinking is enhanced by better carboxylic esterification, as shown by the comparison between C12P and C2P and also by technical results [2] which will be discussed later.

From a structural point of view, the esterification of phosphonic functions appears to take place only when one carboxylic acid function is separated from the phosphonic acid function by two carbon atoms, ie, in a β position. This will also be discussed later.

• *Esterified species*

Examination of the evolution of various species found in the reaction medium as a function of time should help determine the mechanism of phosphonic and carboxylic esterification. When phosphonic esterification is negligible (C1P and C13P), carboxylates are practically the sole products; with C13P, monocarboxylates readily give dicarboxylates.

With C2P (fig 2 and 3) the yields of monocarboxylate, monophosphonate and diester first increase and reach 12–14% after 5 min. Although the variation is slower, the yield of monocarboxylate increases to 30% in 30 min, while the yield of monophosphonate decreases between 15 and 30 min, to reach a rather low constant 10% yield. During this time, the yield of diester increases to > 50%. It follows that the diester is formed from monophosphonate and not from monocarboxylate, so the latter would not be easily esterified on its phosphonic function. This conclusion is in accordance with results obtained when the methyl carboxylate of C2P, prepared independently, is reacted under the same conditions or without a base (table II). After 15 min, only traces of phosphonates were observed (56% for C2P) and a value of 12% is observed after at least 1 h (66% for C2P). During this time, some transesterification takes place with Thol.

In a more acidic medium (with no added NaH), where carboxylic esterification of C2P is easier, the percentage of monophosphonate is lower, as expected.

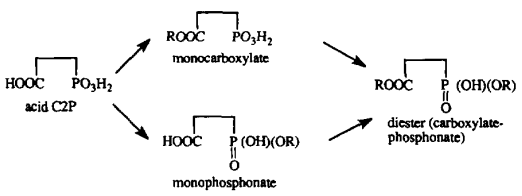

Fig 2. Esters expected from C2P.

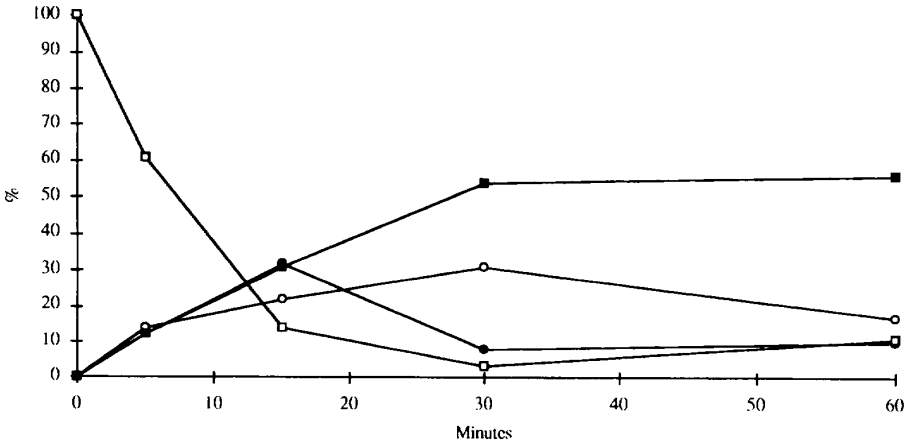

Fig 3. Esterification of C2P by Thol: species as a function of time. –•– Monophosphonate; –○– monocarboxylate; –■– diester; –□– acid.

Table II. Reaction of Thol with C2P methyl carboxylate[a,b].

	P%	*C%*	*Ac%*
5 min	0 (0)	0 (40)	90 (60)
15 min	1 (10)	1 (69)	98 (27)
60 min	12 (35)	36 (83)	52 (10)

[a] See table I; [b] 5 mol of Thol per mol of reagent.

However, surprisingly, monocarboxylate decreases steadily and rather sharply after 5 min. Hydrolysis of the ester could explain this observation.

The study of species produced from C12P did not lead to clear-cut conclusions (fig 4). After 5 min of reaction, β-monocarboxylate predominates (50%); the other monocarboxylate (17%) and phosphonates (three species, 17% as a whole) are present. The ratio between α- and β-monocarboxylates is the reverse of that obtained when C2P and C1P are compared; C12P does not react as if it were the sum of C1P and C2P. Moreover, after 15 min, less than 10% of each monocarboxylate is left, while dicarboxylate reaches 26% and phosphonates 60% (equally divided between mono- and dicarboxylic esters). The formation of dicarboxylate is obviously not high enough to account for disappearance of β-monocarboxylate, and so the latter might be suspected to be an intermediate in the phosphonic esterification. However, the low reactivity of the methyl carboxylate ester of C2P seems to preclude it and leads us to suggest carboxylate ester exchange and/or hydrolysis in the rather acidic medium (two COOH functions) to explain the disappearance of β-monocarboxylate.

When rates of monocarboxylates are compared, large differences appear between C2P and C12P: both the reactivity and the number of sites are connected with rates of carboxylic esterification.

Another interesting result in the esterification of C12P is the similarity of results obtained whatever the acidity.

Esterification by trans-*1,2-cyclohexanediol*

A large number of esters are expected here, for example, species derived from the esterification of either or both alcoholic functions, species in which either one or several molecules of *trans*-1,2-cyclohexanediol and either one or several molecules of acid are involved, and diastereomers and oligomers. In these situations, ^{31}P chemical shifts should vary around the mean values expected from the nature of phosphonic function and the vicinity of the carboxylic or carboxylate group.

The esterification of 1,2-cyclohexanediol produced a large number of ^{31}P signals (> 80 in the case of C2P)

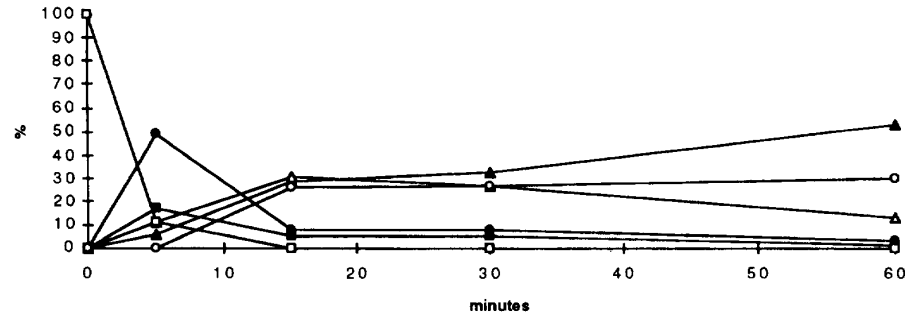

Fig 4. Esterification of C12P by Thol species as a function of time. –▲– Triester; –△– other phosphonate; –•– Monocarboxylate 1; –■– monocarboxylate 2; –○– dicarboxylate; –□– acid.

and it was impossible to establish precise structures or even 'frontiers' between various kinds of phosphonates or, eventually, between mono- and dicarboxylates. Nevertheless, we distinguished clearly two groups of esters: monophosphonates, which may be esterified on the carboxylic functions; and carboxylates (mono- or di-), in which the phosphonic function was not esterified. This provided us with P% rates, global esterification rates and ranges of values for C% rates.

Table III. Esterification of *trans*-1,2-cyclohexanediol (CHD)[a,b].

	Time	
	5 min	*30 min*
$EtPO_3H_2$[c]		
P%	2 (4)	-
Ac%	98 (96)	-
C1P[c]		
P%	- (9)	25 (23)
C%	- (91–100)	75–100 (71–100)
Ac%	0	0
C2P[c]		
P%	53 (44)	66 (59)
C%	15–68 (52–96)	32–84 (39–98)
Ac%	32 (4)	6 (2)
C12P[d]		
P%	39 (29)	64 (53)
C%	58–99 (66–96)	34–100 (44–100)
Ac%	1 (4)	0 (0)

[a] See table I. [b] Lack of identification of esters, C% precise values not known. [c] 5 mol of CHD/total carboxylic and phosphonic function (Z-PO_3H_2 = one function). [d] 7.5 mol of CHD/total carboxylic and phosphonic function (Z-PO_3H_2 = one function).

The global results were similar to those obtained with Thol, with somewhat higher yields (table III). Ethylphosphonic acid reacted poorly, but the phosphonic function of C1P reacted a little better. In the case of C2P, both functions were somewhat more readily esterified by 1,2-cyclohexanediol than by Thol. Higher rates than with Thol were also obtained for C12P, at least for phosphonic esterification. Because we do not know whether esterification proceeds by an intra- or intermolecular reaction (from the diol point of view), it cannot be said whether this result is due to reactivity.

In conclusion, provided hydroxylic functions are physically available to the phosphonocarboxylic acids, both the primary alcohol and the secondary diol of glucose units of cellulose can be esterified during the curing of cotton, ie, both could be involved in crosslinking if they belong to different fibers. Phosphonic esterification appears to be a necessary condition for crosslinking.

Mechanisms of esterification

First we will examine the esterification of phosphonic function. It is well known that direct esterification of phosphonic acids by alcohols does not readily take place [6] as found here for ethylphosphonic acid. It follows that species involving both carboxylic and phosphonic functions should be involved in the reaction pathway for phosphonocarboxylic acids. Mixed cyclic anhydrides are one possibility. Insofar as the positions of the two functions play a major role in esterification, such anhydrides would have to be very easily formed and/or be very reactive towards alcohols due to their specific structures. In both of the favorable cases (C2P and C12P), the supposed anhydrides are five-membered rings, as opposed to six-membered (from C13P) and four-membered (from C1P) rings. The formation of five-membered rings can be thought as the most favorable, as is the case in carboxylic diacid series where five-membered anhydrides promote esterification of acids or hydrolysis of esters with much more efficiency than six- or four-membered cyclic anhydrides, in accordance with enthalpy and entropy considerations [7].

In the phosphonocarboxylic series studied here, factors due to phosphorus itself should also be considered. Mixed five-membered cyclic phosphonocarboxylic anhydrides have been reported [8]. Although we could not isolate the species supposed to be involved in the esterification of C2P or C12P, we prepared the described methyl phosphonate ester of the anhydride derived from C2P. This anhydride was very reactive toward alcohol and water (fig 5).

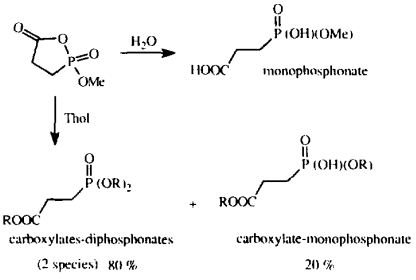

Fig 5. Reactivity of a five-membered cyclic mixed anhydride ester with water and alcohol (Thol, see text) at room temperature. R holds for Me or Th (tetrahydro-2-pyranyl), due to ester interchange.

On the other hand, it is known that five-membered cyclic phosphate and phosphonate derivatives [9] are extremely reactive toward nucleophilic attack, compared with other cyclic or acyclic analogous esters. The explanation relies on well-described characteristic features of phosphoryl (tetracoordinated phosphorus) cyclic compounds. In the case of five-membered rings, nucleophilic attack releases ring tension to give five-membered cyclic alkoxy phosphoranes with pentacoordinated phosphorus. Such phosphoranes, which can be isolated when stabilized by aromatic groups, have well-known configurations, which are in equilibrium through topical rearrangements of substituents [9, 10]. In the most stable configurations, intracyclic P bonds lie in equatorial and apical positions, while alkoxy substituents favor the second apical position, leaving two equatorial bonds of P for hydroxy, alkoxy, alcoholate or alkyl groups (fig 6). For acyclic or six-membered cyclic phosphoryl derivatives, there is no ring tension to favor nucleophilic attack.

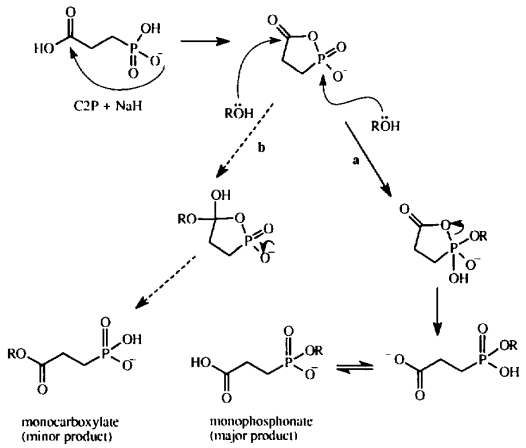

Fig 6. Five-membered cyclic mixed anhydrides as intermediates for the esterification of C2P.

In the absence of aromatic substituents, five-membered cyclic phosphoranes act as reactive intermediates (or activated complexes) if they can be opened readily, which is the case for phosphates and phosphonates, where the apical, intracyclic, polar P-O bond is easily broken, leading to acyclic phosphates or phosphonates. No such opening can occur in the case of phosphinates, which have no intracyclic P-O bond and are much less reactive [9].

When the two requirements are met, ie, release of five-membered phosphoryl ring tension providing a phosphorane ring, followed by breaking of an apical P-O intracyclic bond, an outstanding reactivity is expected. These considerations support the hypothesis of five-membered cyclic mixed anhydrides promoting the esterification of the phosphonic function only in cases of β-carboxylic phosphonic acids such as C2P and C12P (fig 6a), in accordance with the high observed esterification yields. However, no mixed anhydrides could be observed from C2P and C12P after thermal treatment of acids or in esterification mixtures. This was not unexpected for species that are thought to be extremely reactive.

Following the above schemes, carboxylic functions of C2P or C12P could be esterified by concurrent opening of intermediate phosphoranes (fig 6b), although the rather poor reactivity of C2P and C13P and the high reactivity of C1P suggest independent mechanisms.

As expected, carboxylic esterification is generally better performed in acidic medium except, interestingly, in the case of C12P, where a five-membered cyclic carboxylic anhydride promotes carboxylic esterification whatever the acidity. In this case, we observed the carboxylic anhydride after a thermal treatment of C12P followed by IR analysis, contrary to the case of C13P. Carboxylic anhydrides were also observed from two other acids which possess β-carboxylic functions (fig 7c,d). In the same way, it has been reported [11] that when polymeric polycarboxylic acids are heated, carboxylic anhydrides are easily formed from β-polyacids, in contrast with the very small quantities observed from α- or γ-polyacids.

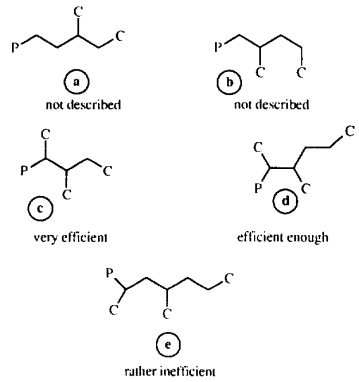

Fig 7. Other phosphonocarboxylic acids and crosslinking of cellulose [2]. (C = COOH, P = PO_3H_2).

However, carboxylic esterification proceeds rather readily for the α-phosphonocarboxylic acid C1P. The reason why the carboxylic functions of C2P and C13P are somewhat less reactive toward esterification is unclear.

Structure, esterification sites and crosslinking

A similar scheme may be drawn for both polycarboxylic and phosphonocarboxylic acids: intermediate cyclic anhydride formation promotes esterification, which causes crosslinking (the outstanding technical results obtained with acid shown on figure 7c are in line with this conclusion). Interestingly, for phosphonocarboxylic acids, no catalyst is needed, as if the phosphonic part of the molecule played the role of an internal catalyst for carboxylic esterification, although catalysis improves technical results in a number of cases.

A question arises whether phosphonic esterification, which was shown to be chemically possible only in the presence of COOH in a β-position related to PO_3H_2, is a necessary condition for crosslinking ability of phosphonocarboxylic acids. The answer is obvious for diacids where the fact that phosphonic esterification cannot occur precludes any crosslinking (compare C1P and C2P). In the case of triacids, such as C12P and C13P, esterification of two carboxylic functions would be enough for crosslinking. Lower rates of carboxylic esterification are observed with C13P, but the difference with C12P is not high enough to be the reason for the technical inefficiency of C13P as a crosslinking agent. The esterification of the phosphonic function thus seems to be the critical factor. The comparison of C13P with C2P, which is a good crosslinking agent easily esterified on the phosphonic function but whose global esterification ability is much lower, also seems to indicate the necessary condition of phosphonic esterification for crosslinking ability. This statement should be ascertained by the examination of other phosphonocarboxylic acids, that can form only one sort of five-membered anhydride. In that respect, the comparison of C13P with an acid such as C34P (fig 7a) and of C12P with an acid such as C24P (fig 7b) would be enlightening. These acids have not been studied to date.

The above schemes hold for a number of known phosphonotricarboxylic acids. Very good and good crosslinking results were obtained [2] with two acids (c and d on fig 7) whose functions are favorably positioned for both carboxylic and phosphonic esterification; carboxylic anhydrides were indeed observed in both cases after thermal treatment, but the esterification rates are unknown. In the same way, the inefficiency of homologues of d in figure 7 (ie, e in fig 7) was expected.

Conclusion

For a number of rather simple phosphonocarboxylic acids, a clear correlation exists between their ability to act as cellulose crosslinking agents and their ability to be esterified on the phosphonic function, provided enough carboxylic esterification can take place. The esterification is clearly connected with structures favoring five-membered cyclic anhydrides, although mixed phosphonocarboxylic anhydrides could not be evidenced.

Experimental section

Typical esterification reaction

(Tetrahydro-2-pyranyl)methanol (Thol, 16 or 32 mmol), acid (3.2 mmol) and maybe sodium hydride (3.2 mmol) were stirred for 2, 5, 10, 15, 30, 50, 60 min or longer at 180 °C. Solvent was added and ^{31}P NMR spectra were recorded. Esters were characterized as described previously [5].

With *trans*-1,2-cyclohexanediol, the esters could not be individually identified but could be classified in two categories by analogy with the results obtained with Thol [5] according to ^{31}P chemical shift increments $\Delta\delta$ of esters related to corresponding acids: phosphonates (more or less esterified on phosphonic function) $\Delta\delta$ +1.1 to +2.7 ppm; and carboxylates (mono- or di-, not esterified on phosphonic function) $\Delta\delta$ −0.1 to −0.6 ppm.

Anhydride formation

A few drops of a water solution of 2-phosphonosuccinic acid C12P were placed on a KBr disc which was heated 4 min on a hot plate at 180 °C. Immediate analysis by FTIR showed two characteristic bands at 1 861 cm^{-1} (weak) and 1 785.5 cm^{-1} (strong) while the large 3 400 cm^{-1} O-H stretching band and the strong 1 717 cm^{-1} C=O stretching band of carboxylic acid C12P had nearly disappeared.

In the same conditions succinic acid provided the corresponding five-membered cyclic anhydride with two characteristic C=O stretching bands at 1 890 cm^{-1} (weak) and 1 785 cm^{-1} (strong). On the other hand, the previously described 2-methoxy-2,5-dioxo-1,2-oxaphospholane [8] shows, as expected for a mixed phosphonocarboxylic anhydride, a single strong C=O stretching band at 1 810 cm^{-1}.

In the same conditions, anhydrides were not observed with glutaric acid or 2-phosphonoglutaric C13P, 2-phosphonoacetic C1P and 2-phosphonopropanoic C2P acids.

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