Conclusions drawn from a study of cellulose nitration in technical mixed acids by X-ray photoelectron spectroscopy and ^{13}C nuclear magnetic resonance

R. D. Short* and H. S. Munro†
Department of Chemistry, Durham University, South Road, Durham DH1 3LE, UK
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The nitration of cellulose in technical mixed acids has been studied by X-ray photoelectron spectroscopy and ^{13}C nuclear magnetic resonance. The study was carried out in order to better our understanding of the nitration mechanism, and of the factors that control the extent of nitration achieved in these mixes. From this work two major conclusions can be drawn: (1) that the nitronium ion, NO_2^+, is the important nitrating species of cellulose; and (2) contrary to previous arguments, fibre crystal structure does play an important role in determining the degree of substitution (*DOS*) achieved, but not as previously envisaged.

INTRODUCTION

Cellulose nitrate is the oldest cellulose derivative, first prepared when cellulose fibres in the form of sawdust, linen and paper were treated with nitric acid[1]. The resulting product has been described as the most important inorganic ester of cellulose and is utilized in a range of industrial applications in areas as diverse as: lacquers (automobile refinish, wooden furniture); inks; plastics and films; the nuclear industry (radiation monitors); microelectronics (resist material); and, perhaps most important, the munitions industry[2].

These days cellulose nitrate is commercially prepared from technical mixed acids, i.e. acid mixes composed of nitric acid, sulfuric acid and water. However, despite the widespread production of cellulose nitrate, and the proliferation of published literature concerned with the nitration of cellulose, a clear picture of the nitration mechanism has yet to emerge. In particular, two issues have not been satisfactorily resolved: (i) the identity of the nitrating species; and (ii) the importance of fibre structure in controlling the extent of nitration.

Molecular nitric acid has, even in recent reviews[2,3], been cited as the effective nitrating species, while in nearly all other fields of organic nitrations the nitronium ion, NO_2^+, is accepted as the nitrating species[4]. A plausible explanation for this divergence in thought is perhaps historical. The results of Ingold's[5] studies on the nitration of organics were published in the middle and late 1950s, whilst the major work on cellulose nitration was carried

out in the 1930s. Miles' comprehensive review of cellulose nitrate chemistry[6] was published in 1955 and does not make reference to the work of Ingold. Although Miles acknowledges the presence of the nitronium ion in mixed acids, he cites the nitric acid molecule as the active species in all nitrations of cellulose. Since Miles' review there has been little interest, until very recently, in the nitration mechanism. Consequently, most recent reviews[2,3] reference the work of Miles and draw similar conclusions about the nitration mechanism, identifying nitric acid as the nitrating species.

Ingold and others established the role of the nitronium ion in aromatic nitrations on the basis of kinetic studies using mixes of high and low nitronium ion concentration[4]. However, similar experiments with cellulose have not been feasible because of the heterogeneous nature of this nitration. Miles and others ruled out the possible involvement of the nitronium ion in the nitration of cellulose on the grounds that: (i) cellulose fibres nitrate in nitric acid vapour; and (ii) nitration occurs in acid mixes (technical or otherwise) where the nitronium ion cannot be spectroscopically detected. These arguments were accepted for over 25 years without question until the recent work of Fowler[7].

The control of the degree of substitution (*DOS*) in technical acid mixes has been the subject of much controversy, with two distinctive 'schools of thought' having emerged. One important factor in determining the *DOS* is the nitration time: it has been shown that *DOS* increases with time, levels off in a plateau and then decreases (over a period of a few days)[2,6]. However, the maximum *DOS* obtained is always well short of the theoretical maximum of 3 and is different for different acid mix compositions. This has resulted in the production of many graphs and tables showing *DOS* as

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* Current address: School of Materials, Sheffield University, Northumberland Road, Sheffield S10 2TZ, UK, and to whom correspondence should be addressed
† Current address: Courtaulds Research, Lockhurst Lane, Coventry CV6 5RS, UK

a function of nitration time and as a function of mix composition[6]. The first 'school' has described the control of *DOS* in terms of the 'accessibility' of the cellulose fibre to the nitrating acid, i.e. the *DOS* is determined by the ability of the acid mix to penetrate the crystal structure of cellulose fibres; and hydroxyls located in crystalline regions are considered to be 'inaccessible' to nitration[6]. The second 'school' has preferred to describe the control of *DOS* in terms of an equilibrium between nitration and denitration[2,8]. However, whilst both arguments, 'accessibility' and 'equilibrium', have been strongly supported by selective observations, neither argument explains all reported observations, and hence the mechanism of control of *DOS* has remained unresolved for over one hundred years[9].

In this paper, new results are presented along with older data and conclusions drawn on the mechanism of nitration and control of *DOS* in technical mixed acids. The influence of fibre structure on nitration has been assessed by directly comparing surface and bulk nitration. This has been achieved by the application of X-ray photoelectron spectroscopy (X.p.s.), in parallel with other spectroscopies, i.e. ^{13}C nuclear magnetic resonance (n.m.r.) and Raman. This multi-technique approach has provided a great deal of new data to enhance our understanding of the complexities of this heterogeneous reaction.

EXPERIMENTAL

Nitration

Whatman No. 1 cellulose papers (unless otherwise stated), cotton linters (Holden Type II) and cellophane (BCL) were nitrated in technical mixed acids and nitric acid/dichloromethane mixes according to the procedures described in ref. 10. The cellophane was prepared by the viscose process. The cellophane was without additives; impurities include < 10 ppm sodium, 10 ppm chloride, and 50 ppm sulfur.

The reagents used in these nitrations were fuming nitric acid (Aldrich Chemical Co), sulfuric acid (98% BDH) and redistilled dichloromethane (May and Baker Ltd).

Spectroscopy

X-ray photoelectron spectra were recorded using a Kratos ES 300 electron spectrometer using Mg Kα X-rays. Spectra were analysed using the software on the Kratos DS 300 data system. N_{1s} and C_{1s} core level intensities were converted into surface *DOS* values using the procedures described in ref. 10.

Raman spectra were recorded on a Varian Carey 82 Raman Spectrometer using an argon gas laser (514.5 nm, 200 mW).

Solution-state ^{13}C n.m.r. spectra were recorded on a Brucker AC 250 MHz spectrometer, proton-noise-decoupled (62 MHz) with typical acquisition times of 9–12 h.

Bulk DOS measurements

The bulk percentage of nitrogen was determined employing a Carlo-Erba Elemental Analyser (MoD 1106), which has been shown to give values in reasonable agreement with those obtained from micro-Kjeldahl analysis (see later section)[10].

RESULTS AND DISCUSSION

The effective nitrating species

In *Table 1* the surface *DOS*, as calculated from C_{1s} and N_{1s} (core level) X.p.s. spectra, are presented as a function of immersion time for cellulose papers nitrated in three different composition acid mixes.

The acid mixes were examined by Raman spectroscopy. In mix 1 the nitronium ion was detected at 1400 cm^{-1}, in mix 2 the nitronium ion was on the verge of spectroscopic detection, and in mix 3 it was not detectable. In mix 1 surface nitration was extremely rapid, with the final *DOS* reached within 1 s. At the other extreme, in mix 3 nitration was negligible after 1 s, although the final surface *DOS* reached at $t = 40$ min was high.

These data, taken along with evidence for nitration in nitronium ion salt solutions[11], further support the view[7] that the nitronium ion is in fact the important nitrating species in technical acid mixes, and not nitric acid. Miles' arguments against the involvement of the nitronium ion in nitration may be countered thus:

(1) Although this ion does not exist in nitric acid vapour, autoionization of adsorbed nitric acid on the fibre will give rise to the nitronium ion:

$$2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O \qquad (1)$$
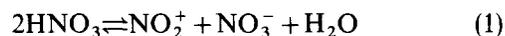
with subsequent nitration.

(2) Although the nitronium ion cannot be detected in acid mixes shown to be capable of nitration, this does not rule out its existence in these mixes and in such cases the kinetics of nitration must be considered.

In many aromatic nitrations, nitration takes place in regimes where the nitronium ion cannot be spectroscopically detected. In such cases the nitronium ion is still considered to be responsible for nitration on the basis of kinetic arguments[4]. We believe the same arguments to apply here. For example, in the nitration of cellulose in low-concentration solutions of nitronium tetrafluoroborate (in sulfolan) the nitronium ion cannot be spectroscopically detected, yet nitration takes place — but at a much slower rate than in mixes of greater nitronium ion concentration[10].

The control of surface DOS

Surface DOS with acid mix composition. Surface *DOS* values were monitored as a function of acid mix composition. Four acid mix compositions were employed and the maximum *DOS* values achieved in each mix are presented in *Table 2*. The maximum *DOS* was reached in these mixes at different rates, but in all mixes a maximum value was reached by $t = 40$ min.

From *Table 2* it can be seen that the maximum *DOS* obtained increased with increasing sulfuric acid content (relative to water) up to a value of $\simeq 65/70\%$ w/v. A slight drop in *DOS* was noted in the 75% w/v sulfuric acid mix, and when the sulfuric acid component in this

Table 1 Surface *DOS* monitored with nitration time

	DOS	
Mix composition	1 s	40 min
Mix 1: 75% H_2SO_4, 23% HNO_3, 2% H_2O	2.3	2.3
Mix 2: 61% H_2SO_4, 23% HNO_3, 16% H_2O	0.995	1.95
Mix 3: 58% H_2SO_4, 23% HNO_3, 16% H_2O	0.1	1.73

mix was replaced by oleum a further depression in *DOS* (→2.1) was observed. From the Raman spectra of these mixes it was evident that the effect of increasing the sulfuric acid content (relative to the water) was to move equilibrium (1) over to the right-hand side (i.e. to increase the proportion of the nitric acid ionized). Assuming that the nitronium ion is the effective nitrating agent, this result then implies that some other agent is limiting the extent of surface nitration.

Table 2 Maximum surface *DOS* with acid mix composition

Mix composition	*DOS*
Mix 1: 75% H_2SO_4, 22.5% HNO_3, 2.5% H_2O	2.3
Mix 2: 70% H_2SO_4, 22.5% HNO_3, 7.5% H_2O	2.4
Mix 3: 65% H_2SO_4, 22.5% HNO_3, 12.5% H_2O	2.35
Mix 4: 60% H_2SO_4, 22.5% HNO_3, 17.5% H_2O	1.9

Two possibilities for incomplete surface nitration in technical acid mixes have been considered: (1) nitration is limited by competitive sulfonation; or (2) competitive denitration by the sulfuric acid limits the nitration.

Sulfonation. The levels of residual sulfur in the surface of the cellulose nitration prepared from mixes 1 and 4 were determined; see *Table 3*. Prior to X.p.s. analysis, these cellulose nitrates were well washed (<6°C), but not boiled with distilled water. This procedure removes adhering acid from the cellulose fibres but does not hydrolyse sulfate esters[6]. From the results presented in *Table 3* it is clear that sulfate formation does not account for 'shortfall' in nitrate *DOS* from the theoretical maximum of 3.

Competitive denitration. Employing X.p.s. it has been possible to study the immersion of cellulose nitrate in concentrated sulfuric acid for short periods. Displayed in *Figure 1* are the C_{1s} and N_{1s} core level spectra of
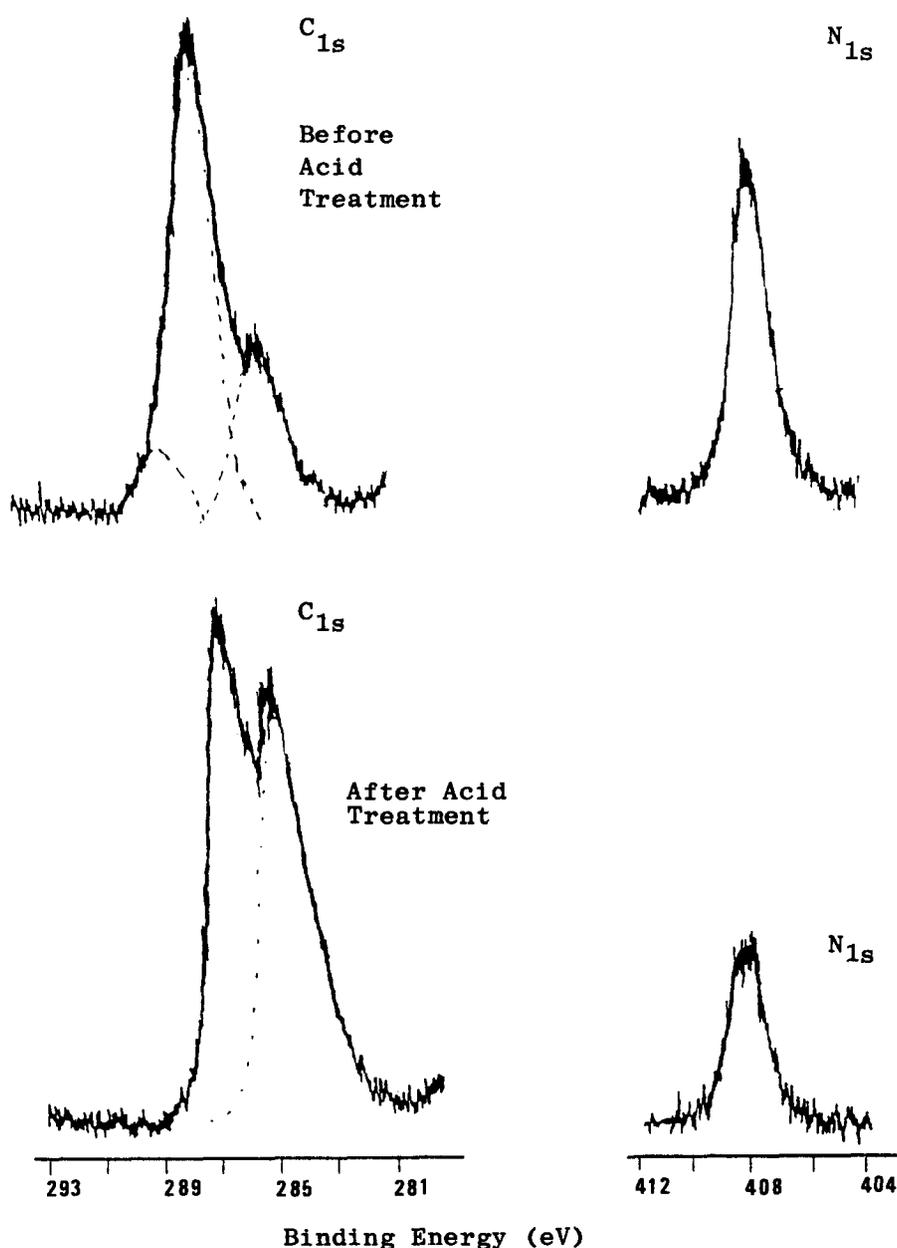

Figure 1 X.p.s. spectra for cellulose nitrate before and after sulfuric acid treatment

Table 3 Degree of substitution (surface)

	ONO_2	OSO_3H
Mix 1	2.3	0.08
Mix 4	1.9	0.04

Table 4 Surface and bulk *DOS* with acid mix composition

Mix composition	Surface DOS	Bulk DOS	Miles
75% H_2SO_4, 22.5% HNO_3, 2.5% H_2O	2.3	2.65	(2.45)
70% H_2SO_4, 22.5% HNO_3, 7.5% H_2O	2.4	2.82	2.76
65% H_2SO_4, 22.5% HNO_3, 12.5% H_2O	2.35	2.78	2.60
60% H_2SO_4, 22.5% HNO_3, 17.5% H_2O	1.9	2.46	2.26

pristine cellulose nitrate and the same cellulose nitrate after immersion in 80% sulfuric acid for 2 min.

Competitive denitration by the sulfuric acid component of technical mixed acids was discounted by Miles[6] on the grounds that bulk denitration was not observed in a 68% sulfuric acid/water mix. In more concentrated mixes cellulose nitrate was found to be irretrievably degraded, and therefore studies in more concentrated mixes were not considered feasible because of the reliance of workers on bulk techniques for monitoring nitrogen content. From the loss of intensity in the nitrogen signal in *Figure 1*, it can be seen that extreme denitration has taken place in an 80% sulfuric acid mix. From this result it has been concluded that strong acids will denitrate cellulose nitrate, and whilst cellulose nitrates are stable in strong acids, celluloses are not.

The reversibility of the nitrating reaction, in technical mixed acids, has been investigated by Stephenson[2]. The effect of immersing a high *DOS* cellulose nitrate in a lower *DOS* mix was studied by X.p.s. At the fibre surface, rapid denitration was observed with the *DOS* falling to that of the mix. (Mix *DOS* = the value to which the mix will nitrate fresh cellulose.) This result adds further support to the view that in technical mixed acids both nitration and denitration take place and the authors believe that at cellulose surfaces final *DOS* is determined entirely by equilibrium.

Implications of surface results in understanding bulk DOS control

Surface versus *bulk* DOS. In this section we consider how the results obtained from monitoring surface nitration may be used to help explain data obtained from bulk nitration studies.

In *Table 4* maximum surface and bulk *DOS* values are compared for cellulose papers nitrated in the four acid mix compositions previously used (*Table 2*); maximum *DOS* values were obtained within 1 h. The maximum surface *DOS* values were reached much faster, but remained constant up to $t = 1$ h.

The trend obtained in bulk *DOS* values is in good agreement with the trend reported by Miles for similar composition acid mixes[6]; however, the values reported here are consistently greater than those reported by Miles. This discrepancy may arise from: differences in stabilization procedure or cellulose source (hence morphology); or from the use of an elemental analyser in this work to determine *DOS*. In most studies, *DOS*

(%N) is determined by Kjeldahl analysis. In this analysis a small error due to absorbed water is introduced; %N is calculated from moles nitrogen titrated and the weight of the cellulose nitrate (including $\simeq 2\%$ absorbed water) digested by acid. In elemental analysis, the sample is combusted and the %C and %N are obtained. From these values *DOS* was calculated, thus avoiding potential error from any absorbed water. The use (advantages and disadvantages) of elemental analysis are further considered in ref. 10.

More importantly, from *Table 4* it can be seen that in all of the cellulose nitrates prepared bulk and surface *DOS* were not the same. Before attempting to explain this result, it is pertinent that we define more carefully what we consider the surface *DOS* values to represent. In order to do this, it is necessary to consider the structure of the cellulose fibre.

The cellulose fibre is built up from thousands of smaller fibres about 2000 Å thick, which in turn consist of much smaller units, microfibrils, of the order of 200–300 Å thick and these of elemental fibrils about 30–60 Å thick[12]; these dimensions may vary considerably according to cellulose source. By i.r. it has been shown that 40–42% of hydroxyls undergo deuterium exchange with deuterium oxide, and it has been suggested that these hydroxyls are located in the surfaces of the elemental fibrils[13]. The remaining hydroxyls are hydrogen bonded in such a fashion that they are inaccessible to exchange. X-ray diffraction data support this argument: the diffuse nature of X-ray patterns being explained by scattering from lattice distortions along the surface of, or periodically across the length of, the elementary fibrils.

We believe the surface *DOS* values reported in *Table 4* to represent the *DOS* of the anhydroglucose units located in the surfaces of the elemental fibrils. Hydroxyls in these units will be immediately accessible to the acid mix. However, in order for the acid mix to reach hydroxyls located in the interior of the elemental fibrils, the various components of the nitrating mix must penetrate the fibre crystal structure.

In explaining the discrepancy between bulk and surface *DOS* we believe the role of the sulfuric acid to be most critical. Warwicker[14] has shown that sulfuric acid cannot penetrate the crystalline regions of cellulose fibres whilst nitric acid can. Hydrogen bonding in the cellulose crystallites gives the crystallites a sheet-like structure and planar molecules may 'slip' between these sheets whilst non-planar molecules cannot. The nitric acid molecule and, more importantly, the nitronium ion are both planar; sulfuric acid is non-planar. In this paper it is shown that concentrated sulfuric acid is a very effective denitrating agent of cellulose nitrate at the fibre surface, and from the studies of Warwicker it follows that the action of sulfuric acid is likely to be limited to the cellulose surface regions and amorphous regions (which may be one and the same). It follows that at the cellulose surfaces (and similar cellulose regions) the presence of sulfuric acid limits the *DOS* achieved. However, in the bulk, i.e. in the cellulose crystallites, sulfuric acid is excluded. Therefore in these regions nitration proceeds as at the surface, but denitration is, to some extent, inhibited. If correct, this would result in uneven nitration throughout the fibre, with a higher *DOS* in the crystalline regions. Such uneven nitration has been previously demonstrated by solution-state ^{13}C n.m.r.[15]. Clark and Stephenson[8] have shown how this technique can be employed to determine the

sequence and substitution distributions of nitrate esters in cellulose nitrates.

Substitution distribution. In *Table 5* the substitution distributions obtained in cellulose nitrates prepared from technical mixed acids and from nitric acid/dichloromethane mixes are compared at equivalent *DOS*.

From *Table 5* it can be seen that whilst the nitrate ester distribution is fairly even among the anhydroglucose units after nitration with the organic acid mixes, the cellulose nitrates prepared from the technical mixed acids display very uneven nitrate ester distribution. For example, in a material of *DOS* 2.1 a high proportion of the anhydroglucose units were found to be trisubstituted (49%), but a substantial number of units remain unsubstituted (17%). We argue that the high proportion of unsubstituted anhydroglucose units originate from the accessible (i.e. surface) regions of the elemental fibrils.

A critical test of the ideas presented above is to compare the nitration of celluloses of different morphology under identical conditions in mixed acids and then to compare surface and bulk *DOS*. From the arguments above we would anticipate surface *DOS* to be unaffected by cellulose morphology, but bulk *DOS* would increase with increasing fibre crystallinity.

Bulk DOS *with crystallinity.* For this experiment three celluloses were selected: cotton linters, papers and a regenerated cellulose cellophane. The crystallinity of these celluloses was tested by a simple sorption experiment; this confirmed the anticipated trend in crystallinity, i.e. linters > papers ≫ cellophane. These celluloses were nitrated in the four mixed acid compositions previously employed. The results for bulk *DOS* are displayed in *Table 6*. From this table it can be seen that the bulk *DOS* achieved does indeed depend on the crystallinity of the material, i.e. the most crystalline cellulose shows the greatest *DOS* for nitration in all mixes, the least crystalline shows the lowest.

Surface *DOS* was only monitored for the celluloses nitrated in mix 1. However, the surface *DOS* monitored (2.25 ± 0.05) was constant for all three celluloses. These, admittedly preliminary, results support the central argument advanced — namely surface and bulk *DOS* are not equal, and this inequality arises from the exclusion of sulfuric acid (an important denitrating agent) from the interior of the elemental fibril.

Clearly, the overall picture must be more complex; we do not comment on the role of water, for example, in controlling *DOS*. The picture presented above is qualitative. Future quantitative experiments could easily be devised to test our model of *DOS* control; if the *DOS* of the interior and exterior of the elemental fibril were known, then overall *DOS* could be predicted from an accurate measurement of the crystallinity of the cellulose employed. At high *DOS* the interior *DOS* ought to be approaching 3, exterior *DOS* could be monitored by X.p.s. and hence overall *DOS* calculated from a knowledge of the fibre structure i.e. crystallinity; calculated *DOS* could then be compared with experiment.

CONCLUSIONS

We have presented data to support the view that in the nitration of cellulose by technical mixed acids surface *DOS* is equilibrium-controlled. The results show that the nitronium ion is the effective nitrating species, and sulfuric acid is the effective denitrating species. In the cellulose bulk the *DOS* reached is ultimately determined by the fibre structure. The control of *DOS* in cellulose nitration has previously been explained in terms of both 'accessibility' and 'equilibria'. It is hoped that this work goes some way towards resolving the conflict between the 'accessibility' and 'equilibrium' arguments.

Table 5 Substitution distribution with *DOS* for cellulose nitrates prepared in different mixes

(a) Nitric acid/dichloromethane mixes

DOS	Anhydroglucose residues (%)				
	2,3,6	2,6	3,6	6	Unsub.
1.95	23	38.5	19	15.5	4
2.19	32	39	16	13	0
2.30	42	33	13	12	0
2.41	50	31	10	9	0
2.81	81	16	3	0	0
3.00	100	0	0	0	0

(b) Technical mixed acid

DOS	Anhydroglucose residues (%)				
	2,3,6	2,6	3,6	6	Unsub.
1.8	36	22.5	15.5	9.5	16.5
2.10	49	18	10	6	17
2.15	53	22	11	6	6
2.40	57	22	9	7	5
2.67	83	11	6	0	0

Table 6 Bulk *DOS* with acid mix compositions

		DOS		
		Linters	Papers	Cellophane
Mix 1:	75% H_2SO_4	2.75	2.65	2.11
Mix 2:	70% H_2SO_4	2.82	2.82	2.62
Mix 3:	65% H_2SO_4	2.82	2.78	2.70
Mix 4:	60% H_2SO_4	2.51	2.46	–

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