

Study of the Nitration of Methyl Cellulose

JACK BOBINSKI and YVON P. CARIGNAN, *Propellant Laboratory,
Picatinny Arsenal, Dover, New Jersey 07801*

Synopsis

A two-step procedure for the preparation of methyl cellulose nitrate is described. The heterogeneity of the methylation step is reflected in the nonuniformity of the products obtained by nitration with either 98% nitric acid or a solution of 98% nitric acid in methylene chloride. On the basis of the experimental data it is calculated that methyl cellulose having a minimum degree of substitution of 1.8 is required for the preparation of a uniformly substituted methyl cellulose nitrate.

INTRODUCTION

Study of the synthesis and evaluation of the physical and chemical properties of methyl cellulose nitrate was undertaken as part of a broad investigation of cellulose derivatives which incorporate into their structure some other functional group in addition to the nitrate function. The preparation of methyl cellulose nitrate has already been reported at least in three instances.¹⁻³ However, these preparations were conducted strictly in an attempt either to characterize partially denitrated cellulose nitrate¹ or as a means to study the uniformity of substitution in methyl cellulose.² In contrast with previous work, the chief concern in the present investigation has been to explore methods of preparation of methyl cellulose nitrate in the hope of obtaining a product with improved chemical, physical, and mechanical properties over cellulose nitrate.

Of the two possible approaches, methylation of cellulose nitrate or nitration of methyl cellulose, the latter was judged more promising for a number of reasons. On the one hand, demethylation is not anticipated to occur³ during nitration while denitration is known to proceed significantly during the strongly basic conditions of the conventional methylation reaction.² Furthermore, in considering the preparation of methyl cellulose nitrates covering a broad range of substitution in both methoxy and nitrate groups, a better control of the substitution could be achieved by first methylating cellulose followed by nitration of the partly methylated cellulose. In the present communication a brief description of the preparation of methyl cellulose of various degrees of substitution is presented followed by a more detailed description of the nitration step which was carried out either with 98% nitric acid alone or a 98% nitric acid solution in methylene chloride.

RESULTS AND DISCUSSION

Preparation of Methyl Cellulose

Methyl cellulose was prepared essentially following the procedure originally reported by Haworth.⁴ Since one of the objectives was to compare methyl cellulose nitrate to cellulose nitrate military grade (12.6% N, degree of polymerization 250–350) in regards to mechanical properties obviously the degree of polymerization (DP) of the former had to be in the neighborhood of 300 for a self-consistent comparison. Consequently, conditions for the methylation of cellulose DP 1470 had to be so chosen as to yield a methyl cellulose having a DP in the neighborhood of 500 in prevision of the nitration step which was anticipated to degrade the chains further. No doubt the DP of methyl cellulose is controlled primarily by the time of contact of cellulose with sodium hydroxide during the preparation of the intermediate alkali cellulose. Information as to the rate of the cellulose chains degradation was extracted from the work of Timell and Purves³ who measured the changes in DP during aging of alkali cellulose under conditions comparable to those used in the present study. The time required to bring the DP down to approximately 500 was estimated to be 17 hr. on the basis of their data.

The time of reaction was kept constant at 17 hr., and a number of methyl celluloses with degrees of substitution (DS) ranging from 0.15 to 1.40 were prepared by varying the quantity of dimethyl sulfate in the medium as shown in Table I. The shape of the substitution–dimethyl sulfate concentration curve (Fig. 1) is indicative of the heterogeneity of the reaction. In line with the conclusions reached by Timell and Purves³ it is quite apparent that the initial stages of the methylation under the conditions prevalent in this study consist mainly in the substitution of the low molecular weight components of the accessible regions which were subsequently removed during the isolation of the product. The apparent discontinuity in the shape of the curve at about DS 0.8 may, of course, represent a real

TABLE I
Methylation of Cellulose with Dimethyl Sulfate^a

Dimethyl sulfate, mole	Product methyl cellulose (DS)
0.15	0.15
0.30	0.39
0.45	0.54
0.60	0.67
0.75	0.74
1.05	1.08
1.20	1.26
1.50	1.40

^a Cellulose, 50 g. (0.3 mole); solvent, toluene; base, 40% NaOH; reaction time, 17 hr.; reaction temperature, 25°C.

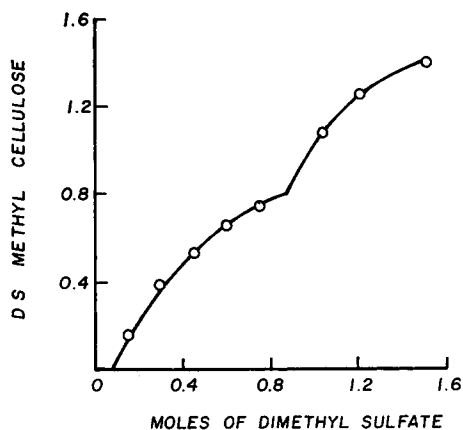


Fig. 1. Methylation of cellulose with dimethyl sulfate. Reaction time, 17 hr.

TABLE II
Fractionation of Methyl Cellulose, DS = 1.40*

Solvent	Extract weight, g.	% Extracted	Extract DS
Methylene chloride	0.13	4.3	2.23
Water	0.73	24.3	0.95
Residue	1.95	65.0	1.44

* Sample weight, 3.00 g.; material balance, 94%.

change in the methylation process, from a predominantly micellar-heterogeneous to permutoid,³ at which point the reagent begins to penetrate between the chains of the crystalline region. However, at this stage the substitution is still far from being uniform, and in fact even at high DS (1.4), nonuniformity of substitution still persists, as shown in the fractionation data of Table II.

Nitration of Methyl Cellulose with 98% Nitric Acid

Nitration of a commercial methyl cellulose (Methocel, Dow Chemical Co.) of DS 1.75 by this procedure lead to some interesting observations. As shown by the data of Table III nitration of the free hydroxyl groups proceeds very fast, being more or less completed within 10 min. Soon after the addition of methyl cellulose to the nitrating medium a clear solution resulted. Timell and Purves,³ in the course of their nitration study of technical grade methyl cellulose of DS 1.78 have observed only partial solubility of the product methyl cellulose nitrate in the nitrating medium which consisted of nitric acid-phosphoric acid-phosphorus pentoxide. Since their product, which had been nitrated under conditions well known not to degrade the chains, was found to have a DP of 60, it may be inferred that the methyl cellulose nitrate of the present study has a DP not greater than 60 and probably sub-

TABLE III
Nitration of Methyl Cellulose with 98% Nitric Acid^a

Nitration time, min.	Nitration temperature, °C.	Product DS	
		ONO ₂	OCH ₃
10	25	1.2	1.7
30	25	1.3	1.6
60	25	1.3	1.6
120	25	1.4	1.5

^a Technical methyl cellulose (Methocel), DS = 1.75

stantially lower as a result of the degradative nature of 98% nitric acid. Although no attempt has been made to determine the DP of the products, the remarkably low intrinsic viscosities found in acetone (0.09–0.30 dl./g.) point to the fact that the DP is very low. Increasing the time of nitration from 10 min. to 2 hr. lowers the methoxy content slightly with a corresponding rise in the nitrate content.

Nitration of methyl cellulose (DS 0.50) appears to follow a different course. For one thing, most of the methyl cellulose nitrate did not dissolve in the nitrating medium. In addition, the degree of methoxy substitution in the product was only 0.10. These results prompted a closer look at this reaction and a serious attempt was made to obtain a material balance of both product and unreacted methyl cellulose. The results shown in Table IV show very clearly that the starting methyl cellulose was heterogeneous

TABLE IV
Nitration of Methyl Cellulose (DS = 0.50) with 98% Nitric Acid^a

Product	Weight, g.	DS		Recovery, %
		ONO ₂	OCH ₃	
Soluble in HNO ₃	0.20	1.90	0.90	2.7
Insoluble in HNO ₃	6.10	2.50	0.10	72.2
Unrecovered	1.26 ^b	—	1.76 ^b	25.1 ^b

^a Reaction time, 30 min.; reaction temperature, 25°C.; sample, 5.00 g.

^b Calculated.

to the extent that approximately 70% of this material is essentially unsubstituted. Evidently the methylating agent has not penetrated beyond the most accessible region which consists apparently of low molecular weight fractions.

Nitration of Methyl Cellulose with 98% Nitric Acid in Methylene Chloride

A modification of the nitration procedure was adopted which consisted in diluting the 98% nitric acid with methylene chloride and performing the nitration at the boiling point of the solvent. These conditions would be more favorable to minimize the degradation of the chains. In one series of

TABLE V
Nitration of Methyl Cellulose with 98% Nitric Acid in Methylene Chloride^a

Methyl cellulose DS	Insoluble product DS		Insoluble product yield, %
	ONO ₂	OCH ₃	
0.15	2.57	0.08	100
0.39	2.55	0.10	
0.54	2.52	0.07	72
0.67	2.53	0.17	
1.08	2.47	0.14	
1.10	2.43	0.17	
1.26	2.43	0.18	
1.40	2.53	0.22	23

^a Reaction time, 60 min.; reaction temperature, reflux.

experiments a number of methyl celluloses covering a wide range in substitution (DS 0.15–1.40) were nitrated for 1 hr. (Table V). In every case it was observed that the product of the reaction was distributed into a soluble fraction and an insoluble fraction in the reaction medium. The distribution was found to be a function of the DS of the starting methyl cellulose. For each methyl cellulose studied, the insoluble product was essentially cellulose nitrate, the substitution in methoxy being of the order of 0.20 or less. So even, the highly substituted methyl cellulose (DS 1.40) is heterogeneous in nature. This is more clearly seen in the experiment described in Table VI, where it is found that the average degree of methoxy substitution of the two fractions ranges from 0.20 to 1.80. Comparison of Tables IV and VI leads to the interesting observation that for both methyl celluloses, DS = 0.50 and DS = 1.40, the lost fractions are comparable in regards to methoxy substitution and in their respective amount. Since the insoluble material in the nitrating medium was in all instances found to contain very low content of methoxy group, the quantity of this material in any given experiment could possibly be directly related to the extent of penetration of the methylating agent in the cellulose fiber. Drawing from the data of Table V and plotting per cent insolubles versus degree of methoxy substitution gives an extrapolated value of 1.8–1.9 for an hy-

TABLE VI
Nitration of Methyl Cellulose (DS = 1.40) with 98% Nitric Acid in Methylene Chloride^a

Product	Weight, g.	DS		Recovery, %
		ONO ₂	OCH ₃	
Soluble in HNO ₃	2.42	1.0	1.8	48.4
Insoluble in HNO ₃	1.16	2.3	0.2	23.2
Unrecovered	1.42	—	1.70 ^b	28.4 ^b

^a Reaction time, 30 min.; reaction temperature, reflux; sample, 5.00 g.

^b Calculated.

pothetical methoxy substitution at which no insoluble would be found in the nitrating medium. In other words, methyl cellulose of $DS = 1.8$ could be regarded as the threshold value in substitution which would lead to a homogeneous product. This, of course, applies only for the heterogeneous methylation procedure used in this study.

EXPERIMENTAL

Reagents

Wood pulp cellulose MMS Raycol 261-A, DP 1476 (Rayonier, Inc., Whippany, N. J.) was used as received. Similarly, dimethyl sulfate supplied by Matheson Coleman & Bell was used as received. Nitric acid (98%) was obtained from Allied Chemical Co., Morristown, N. J.

Preparation of Methyl Cellulose

Dried wood pulp cellulose, 50 g. (0.3 mole) was treated with 40% aqueous sodium hydroxide at room temperature for 40 min. The excess of sodium hydroxide was then removed by suction while protecting the alkali cellulose from atmospheric oxygen by means of a rubber sheet. To a suspension of alkali cellulose in 2000 ml. of toluene a predetermined amount of dimethyl sulfate was added. The amount of dimethyl sulfate used was determined by the DS of the product desired, varying from 0.15 to 1.50 mole. After the mixture had been kept at room temperature for 17 hr., toluene was removed on a suction funnel, the solid washed with boiling water until completely free of toluene, and then air dried. Methoxyl determinations of the products were done by the Viebock modification of the Zeisel method.⁵

Nitration of Methyl Cellulose with 98% Nitric Acid

The general procedure adopted was to add methyl cellulose to 98% nitric acid kept at 25°C. in the proportion of 20 ml. HNO_3 /g. methyl cellulose. Both the type of methyl cellulose ($DS = 0.15-1.75$) and nitration time (10-120 min.) were varied from experiment to experiment.

When a highly substituted methyl cellulose such as Methocel ($DS = 1.75$) was used as the starting material, a clear solution resulted shortly after addition under agitation. After keeping at 25°C. for a given time with occasional stirring, the solution was poured slowly into ice water to precipitate the product. The product was separated by filtration, washed with water and aqueous sodium carbonate, and then subjected to a stabilization treatment consisting of boiling with a 0.1% aqueous sodium carbonate solution for 120 min. three times. Finally the product was washed with water and dried under reduced pressure at 50°C.

With methyl celluloses of lower substitution ($DS = 0.15-1.40$) as the starting material, no true solution occurred during the nitration step, and consequently the working up procedure was modified as follows. At completion of the nitration the mixture was cooled, decanted, and the solid

residue washed with methylene chloride to remove any residual acid and soluble material.

This solid insoluble material was washed with water and aqueous sodium carbonate solution, followed by the stabilization treatment mentioned above, washed again with water, and finally dried under vacuum.

The decanted nitric acid solution was poured into ice water and the white precipitate separated by filtration. This precipitate was combined with the residue of the methylene chloride liquors (see below), washed, stabilized, and dried as described above.

The methylene chloride liquors were washed with aqueous sodium carbonate solution followed by a water rinse and then evaporated. The solid residue was then combined with the precipitate of the decanted nitric acid solution.

Nitration of Methyl Cellulose with 98% Nitric Acid in Methylene Chloride

The nitrating medium was prepared by adding 98% nitric acid to methylene chloride in the ratio of 1:4 by volume. To this solution was added methyl cellulose in the proportion of 1 g. methyl cellulose/10 ml. nitric acid. The mixture was immediately brought to reflux for a given period of time (15–60 min.). From this point on the work-up procedure was as described above.

All methyl cellulose nitrates prepared in this study were analyzed for their content in both methoxyl and nitrate groups by using established analytical methods.^{5,6}

CONCLUSION

The two-step procedure described in this study for the preparation of methyl cellulose nitrates would be of practical value only in those instances where it is desired to obtain a product containing a minimum methoxy substitution of 1.8. Due to the preponderantly heterogeneous nature of the methylation step, nitration of low-substituted methyl celluloses ($DS < 1$) would yield as much as 50% of a product which for all practical purpose could be considered as cellulose nitrate ($DS_{OCH_3} < 0.2$).

The authors wish to express their gratitude to E. Jones for his assistance in the preparative phase of this study, to D. Farrell, N. Gelber, and J. Jarrell for their contribution in the characterization of the products.

We are grateful to Rayonier, Inc., Whippany, N. J., for supplying the cellulose used.

References

1. G. H. Segall and C. B. Purves, *Can. J. Chem.*, **30**, 860 (1952).
2. E. L. Falconer and C. B. Purves, *J. Am. Chem. Soc.*, **79**, 5308 (1957).
3. T. E. Timell and C. B. Purves, *Svensk Papperstidn.*, **54**, No. 9, 303 (1951).
4. W. N. Haworth, *J. Chem. Soc.*, **107**, 8 (1915).
5. R. L. Whistler, *Methods in Carbohydrate Chemistry*, Vol. III, Academic Press, New York, 1963, pp. 277–80.
6. R. H. Pierson and E. C. Julian, *Anal. Chem.*, **31**, 589 (1959).

Résumé

Un procédé à deux étapes pour la préparation de nitrate de cellulose méthylée est décrit. L'hétérogénéité de l'étape de méthylation entraîne une non-uniformité des produits obtenus par nitration avec soit l'acide nitrique à 98% ou en solution avec l'acide nitrique à 98% dans le chlorure de méthylène. Sur la base des résultats expérimentaux, on calcule que la méthyle cellulose ayant un degré minimum de substitution de 1.8 est indispensable dans la préparation de nitrate de cellulose méthylée substituée uniformément.

Zusammenfassung

Ein Zweistufenverfahren für die Darstellung von Methylcellulosenitrat wird beschrieben. Die Heterogenität des Methylierungsschrittes spiegelt sich in der Uneinheitlichkeit der bei Nitrierung mit 98%iger Salpetersäure oder einer Lösung 98%iger Salpetersäure in Methylenchlorid erhaltenen Produkte. Auf Grundlage der Versuchsergebnisse wird berechnet, dass zur Darstellung eines einheitlich substituierten Methylcellulosenitrates Methylcellulose mit einem Mindestsubstitutionsgrad von 1,8 erforderlich ist.

Received September 8, 1966
Prod. No. 1499