The Reaction of Trityl Salts with 2-Methyltetrahydrofuran and with Tetrahydrofuran[1]

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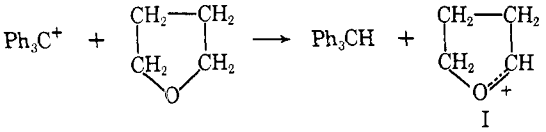
ABSTRACT: The reaction of trityl salts with 2-methyltetrahydrofuran and with tetrahydrofuran (THF) is a dehydrogenation reaction leading to triphenylmethane, a protonic acid, and a furan or dihydrofuran. The acid complexed with monomer is the true initiator of THF polymerization. Consequently, the polymer formed should have hydroxyl end groups on at least one end. Initiation of THF polymerization by diazonium salts probably occurs by a similar mechanism. The conclusions are based on an nmr study of the products of the reaction of Ph_3CSbCl_6, Ph_3CPF_6, Ph_3CClO_4, 4-$ClC_6H_4N_2PF_6$, or Et_3OPF_6 with 2-methyltetrahydrofuran and with THF.

Trityl salts are generally useful as initiators of the polymerization of cyclic ethers.

The use of trityl hexachloroantimonate as an initiator for tetrahydrofuran (THF) polymerization was first reported by Bawn and coworkers.[2] Trityl salts have since also been used to initiate polymerization and copolymerization of trioxane and related cyclic ethers.[3,4]

The mechanism of initiation with these salts has been studied by Bawn, *et al.*,[5] and by Kuntz.[6] This work has shown conclusively that the trityl cation abstracts a hydride ion from THF to form triphenylmethane. The cation formed from THF as a result of this reaction has been formulated as the reasonance stabilized species I shown in eq 1.



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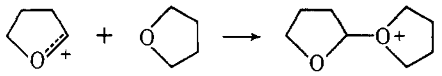
(1)

Initiation of polymerization was then supposed to proceed by reaction of THF at either of the carbons α to the oxygen. Bawn and Kuntz have favored reaction at the α-CH carbon and formation of an acetal end group (eq 2). Kuntz, in fact, reports nmr data which he says supports eq 2.



(2)

In our preliminary report we suggested that I is unstable and readily loses a proton. We have expanded this study and now present the data which we feel confirm our original suggestion.

Experimental Section

Trityl Salts. Trityl hexachloroantimonate (Ph_3CSbCl_6) was prepared from trityl chloride and antimony pentachloride according to the method of Sharp and Sheppard.[7] Carbon tetrachloride was used as the reaction medium instead of benzene.

Trityl perchlorate (Ph_3CClO_4) was prepared by the method of Hofman and Kirmreuther[8] from triphenylmethanol and 70% perchloric acid in a mixture of acetic anhydride and acetic acid.

Trityl hexafluorophosphate (Ph_3CPF_6) was very readily prepared by the second method. Triphenylmethanol (5.2 g) was dissolved at 55° in a mixture of 25 ml of acetic anhydride and 15 ml of glacial acetic acid. Hexafluorophosphoric acid (65%, 4 ml) was added while stirring. The temperature was maintained at 40–50° with external cooling. After the addition of the HPF_6 the slurry was cooled. The product was worked up under a stream of dry nitrogen. The supernatant liquid was decanted from precipitated product and the solids were washed several times with anhydrous ether. After vacuum drying the yield was 6.7 g (86%).

Monomers and Solvent. Tetrahydrofuran and 2-methyltetrahydrofuran were purified by refluxing over metallic potassium under a nitrogen blanket. They were considered sufficiently pure and were distilled when the sodium naphthalene complex formed readily in a small amount of distillate.

Methylene chloride (CH_2Cl_2) was refluxed over calcium hydride for at least 12 hr prior to distillation from calcium hydride under nitrogen.

Nmr spectra were obtained on a Varian A60 instrument at room temperature. The reactions were generally carried out in nitrogen-purged nmr tubes. The tubes were shaken until a uniform solution was obtained.

Results

The majority of our experiments were carried out with 2-methyltetrahydrofuran (2-MeTHF). The reasons for doing this were twofold. First, 2-MeTHF does not polymerize; otherwise 2-MeTHF should behave just like THF. Thus it was possible to obtain simpler spectra of the products of the reaction of 2-MeTHF with the trityl salts. Second, the methyl group might act as a convenient spectroscopic "handle" for following the course of the reaction.

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(1) Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966; *Polym. Preprints*, 7, 413 (1966).

(2) C. E. H. Bawn, R. M. Bell, and A. Ledwith, Chemical Society Anniversary Meeting, Cardiff, 1963.

(3) M. B. Price and F. B McAndrew, *Polym. Preprints*, **7**, 207 (1966).

(4) B. J. K. Smith, J. A. Dodd, A. T. Instone, and D. B. Partridge, *J. Polym. Sci., Part B*, **5**, 625 (1967).

(5) (a) C. E. H. Bawn, R. M. Bell, and A. Ledwith, *Polymer*, **6**, 95 (1965); (b) C. E. H. Bawn, C. Fitzsimmons, and A. Ledwith, *Proc. Chem. Soc.*, 391 (1964); (c) C. E. H. Bawn, R. M. Bell, C. Fitzsimmons, and A. Ledwith, *Polymer*, **6**, 611 (1965).

(6) I. Kuntz, *J. Polym. Sci., Part A-1*, **5**, 193 (1967).

(7) D. W. A. Sharp and N. Sheppard, *J. Chem. Soc.*, 674 (1957).

(8) D. A. Hofman and H. Kirmreuther, *Chem. Ber.*, **42**, 4856 (1909).

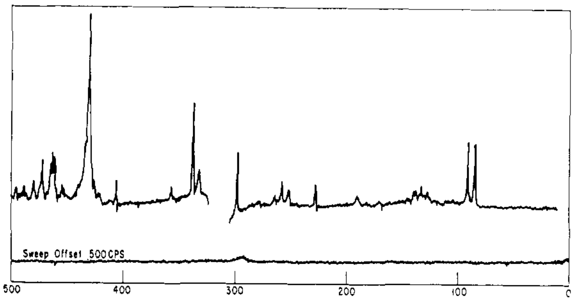


Figure 1. Nmr spectrum of Ph_3CSbCl_6 treated with 2-MeTHF in CH_2Cl_2 solvent. The solvent peak is not shown because it is too strong at the amplification used.

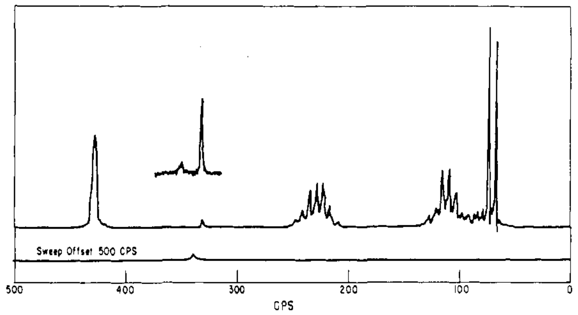


Figure 2. Nmr spectrum of Ph_3CSbCl_6 in bulk 2-MeTHF.

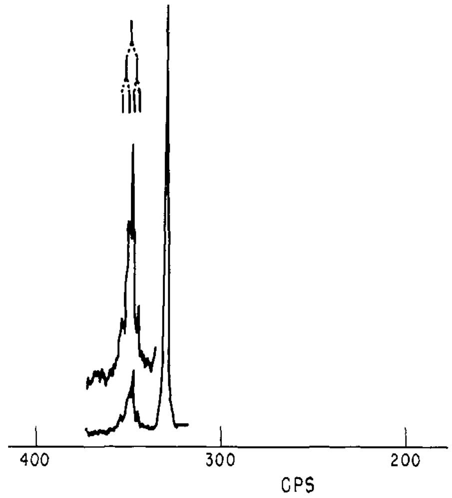
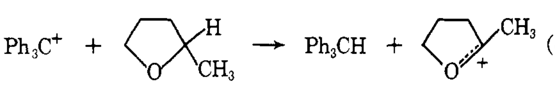


Figure 3. A portion of the spectrum shown in Figure 2 in which the signal has been enhanced with the aid of a time-averaging computer.

Ph_3CSbCl_6 with 2-MeTHF in CH_2Cl_2. When 5×10^{-4} mol of Ph_3CSbCl_6 was allowed to react (1 hr) with 6.4×10^{-4} mol of 2-MeTHF in 0.7 ml of CH_2Cl_2, the nmr spectrum (Figure 1) clearly confirmed the formation of triphenylmethane (Ph_3CH) as observed by Kuntz. Significantly, all of the trityl salt did not react. Unreacted salt was clearly visible in the nmr tube as undissolved powder. As seen in Figure 1, the spectrum showed a typical aromatic pattern slightly downfield from the peak due to the aromatic protons of Ph_3CH. This pattern was consistent with Ph_3C^+ and was therefore assigned to unreacted Ph_3CSbCl_6. The hydride ion needed to form Ph_3CH is extracted from 2-MeTHF and should be largely the hydrogen on the 2-carbon. Hence the methyl doublet in the nmr spectrum of 2-MeTHF should become a singlet (eq 3).



(3)

We observed no evidence for a methyl singlet (Figure 1) and in fact the upfield pattern and areas were consistent with shifted but virtually intact 2-MeTHF. However, integration suggested less 2-MeTHF with respect to Ph_3C (total) than had been charged. In addition, another peak, corresponding to approximately one proton, was observed over 700 cps downfield from the center of the methyl doublet. Thus, a greatly deshielded proton was also formed in this reaction.

The formation of this greatly deshielded proton also serves to explain the downfield shift of the 2-MeTHF peaks. Rapid chemical exchange of the greatly deshielded proton would effect all 2-MeTHF molecules and would result in a single but shifted 2-MeTHF spectrum.

If 2-MeTHF was allowed to react with Ph_3CSbCl_6 in the molar ratio 2:1, all of the trityl salt reacted to give Ph_3CH. The nmr spectrum showed 2-MeTHF and Ph_3CH in a ratio of 1.4:1. In addition, 1 mol of the greatly deshielded proton was formed per mole of Ph_3CH.

Ph_3CSbCl_6 with Bulk 2-MeTHF. In this case 6.85×10^{-4} mol of Ph_3CSbCl_6 and 7×10^{-3} mol of 2-MeTHF gave the spectrum shown in Figure 2. The greatly deshielded proton was 770.5 cps downfield from the center of the methyl doublet. In addition, a weak absorption was noted just downfield from the methine proton of Ph_3CH. This absorption along with that of the methine proton was enhanced using a time-averaging computer and the result is shown in Figure 3. Comparison of the quartet shown in Figure 3 with a spectrum of a substituted furan showed that this quartet could be associated with the proton of the 4-carbon of a 2-substituted furan nucleus. It was not possible to identify more of the furan molecule. The rest of the furan protons would not be shifted downfield as much as the one observed and would probably be under or near the peaks for the protons α to oxygen in 2-MeTHF.

Ph_3CSbCl_6 with THF in CH_2Cl_2. When Ph_3CSbCl_6 was allowed to react with THF in methylene chloride, observations similar to those with 2-MeTHF were made. The greatly deshielded proton was again formed. In this case, somewhat more than 2 mol of THF was required to effect complete reaction of the trityl salt and in addition almost 1 mol of THF per mole of trityl salt charged disappeared. This experiment also verified our assumption that it is valid to extrapolate our results with 2-MeTHF to THF.

Ph_3CSbCl_6 with Bulk THF. Ph_3CSbCl_6 (7×10^{-4} mol) was allowed to react with 0.7 ml (8.6×10^{-3} mol) of THF. In agreement with Kuntz[6] the nmr spectrum showed the presence of Ph_3CH, THF and polytetrahydrofuran. In addition, a peak corresponding to a single proton was seen far downfield. In contrast to Kuntz's observations, we did not find any evidence for an acetal proton. It should be noted that our experiment was run at approximately four times the Ph_3CSbCl_6 concentration used by Kuntz. If the acetal

TABLE I

COMPARISON OF INITIAL AND FINAL RATIOS OF 2-RTHF AND PH_3C GROUP

			Calcd from charge		
Gegenion	R	RTHF/Ph_3C ratio by nmr	RTHF/ Ph_3C^+	(RTHF − $^1/_2Ph_3C^+$)/ Ph_3C^+	(RTHF − Ph_3C^-)/ Ph_3C^+
$SbCl_6^-$	CH_3	1.42	2.02	1.52	1.02
$SbCl_6^-$	CH_3	9.52	10.01	9.65	9.15
PF_6^-	CH_3	6.01	6.98	6.47	5.97
ClO_4^-	CH_3	5.48	6.26	5.77	5.27
$SbCl_6^-$	H	11.30	12.40	11.93	11.43

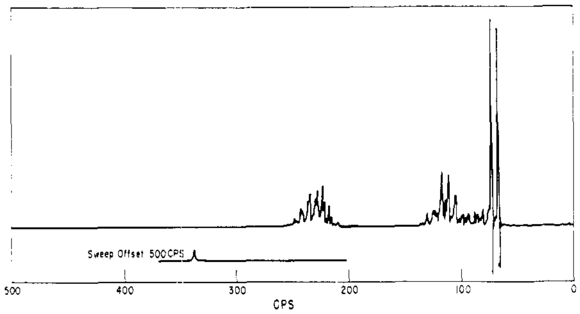


Figure 4. Nmr spectrum of the reaction product of $SbCl_5$ and HCl in 2-MeTHF.

were present in the concentration suggested by Kuntz, it should have been clearly visible under these conditions.

There is a very weak peak in the region of 4.9 ppm. But there also is a similar peak at approximately 2.5 ppm. In our judgment these peaks are most probably ^{13}C satellite peaks of the methylene protons α to the oxygens of THF and polytetrahydrofuran.

The far downfield peak was still present after 5 hr at room temperature. At this time about 45% of the THF had polymerized. However, the far downfield peak had shifted upfield some 30 cps from its position when measured early in the experiment. This peak had broadened considerably. Its area had changed little. This behavior is consistent with the formation of hydroxyl end groups.

Anhydrous HCl in Bulk 2-MeTHF. The nmr spectrum of approximately 10^{-3} mol of anhydrous HCl in 10^{-2} mol of 2-MeTHF had a sharp peak associated with the acid proton 405 cps downfield from the center of the methyl doublet. Thus the far downfield peak cannot be associated with the formation or presence of HCl.

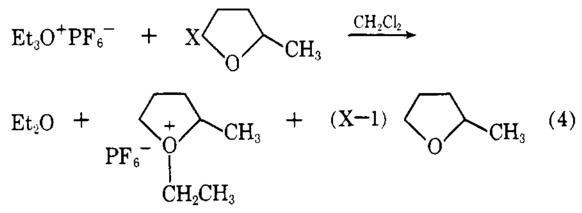
$HSbCl_6$ in 2-MeTHF. Hexachloroantimonic acid ($HSbCl_6$) has previously been prepared from HCl and $SbCl_5$ in ether.[9] The nmr spectrum (Figure 4) of a solution obtained by reacting 10^{-3} mol of $SbCl_5$ with 10^{-3} mol of anhydrous HCl in 10^{-2} mol of 2-MeTHF by slowly warming the mixture from −78° showed a sharp peak approximately equivalent to one proton 769.5 cps downfield from the center of the methyl doublet. In addition the pattern of the protons α to oxygen in 2-MeTHF and the general downfield shift of the 2-MeTHF absorptions corresponded very well with that observed when 2-MeTHF reacted with Ph_3CSbCl_6 (see Figure 2).

Ph_3CPF_6 with 2-MeTHF. The nmr spectrum of 7.2×10^{-4} mol of Ph_3CPF_6 treated with 5×10^{-3} mol of 2-MeTHF in 0.5 ml of CH_2Cl_2 again showed the formation of Ph_3CH. In addition the far downfield peak was again clearly present. The peak was 730.0 cps downfield from the center of the methyl doublet.

Ph_3CClO_4 with 2-MeTHF. The nmr spectrum of 8.0×10^{-4} mol of Ph_3CClO_4 treated with 5×10^{-3} mol of 2-MeTHF in 0.5 ml of CH_2Cl_2 also showed the formation of Ph_3CH. The far downfield peak was present 777.0 cps downfield from the center of the methyl doublet.

$4\text{-}ClC_6H_4N_2PF_6$ with Bulk 2-MeTHF. The solubility of 4-chlorophenyldiazonium hexafluorophosphate ($4\text{-}ClC_6H_4N_2PF_6$) in 2-MeTHF with or without CH_2Cl_2 was too limited to effect reaction at room temperature. Thus 3.5×10^{-3} mol of the diazonium salt was allowed to react with 5×10^{-2} mol of 2-MeTHF for 1 h-at 75°. The nmr spectrum of this solution was measured after standing overnight. The spectrum showed peaks which could be associated with chlorobenzene and with a highly acidic proton.

Triethyloxonium Hexafluorophosphate with 2-MeTHF in CH_2Cl_2. A solution of 8.2×10^{-4} mol of triethyloxonium hexafluorophosphate[10] in 1 ml of CH_2Cl_2 was allowed to react with 1 ml (10^{-2} mol) of 2-MeTHF. The nmr spectra of the two liquid phases which resulted could be fully interpreted in terms of eq 4. There was no evidence for the greatly deshielded proton in this case. This clearly suggests that the presence of the acidic protons is a function of the reaction with trityl salts and is not in anyway characteristic of the oxonium ion–gegenion complex.



(4)

Comparison of Consumption of the Tetrahydrofuran for the Different Gegenions. The nmr spectra above suggested different amounts of THF or 2-MeTHF were consumed in the reactions with trityl salts. The data calculated from the spectra are summarized in Table I. In this table the ratio in the completely reacted mixture of the THF (or 2-MeTHF) to the Ph_3C– group is compared with three ratios calculated from the quantities charged in the experiment. Clearly

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(9) F. Klages, H. Meuresch, and W. Steppich, *Ann.*, **592**, 81 (1955).

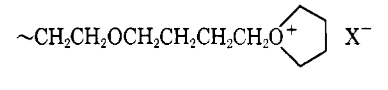
(10) P. Dreyfuss and M. P. Dreyfuss, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, L35.

some tetrahydrofuran is consumed in the course of the reaction. Compare column 3 with column 4.

Discussion

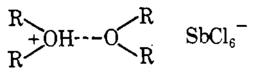
Hydride ion transfer to triphenylmethyl cation is a well-established reaction that has been reviewed and explored by Meerwein.[11] He points out that the reduction of triphenylmethyl chloride by ether in the presence of zinc chloride which Gomberg reported in 1913[12] is an example. The reaction of trityl salts with cycloheptatriene reported in 1957[13] is another example. Kuntz[6] has shown that hydride ion transfer is also the mode of reaction of trityl cation with THF.

What happens after the hydride ion is abstracted from THF and how the polymerization of THF is then initiated is the subject of this paper. The active center in THF polymerization is the trialkyloxonium ion. Thus



any initiation mechanism must generate a trialkyloxonium ion.

The evidence presented above clearly suggests that hexachloroantimonic acid is one of the products of the reaction of Ph_3CSbCl_6 with 2-MeTHF or THF. Especially significant is the correspondence of the location in the nmr spectrum of the greatly deshielded proton with that of the proton of the acid synthesized from HCl and $SbCl_5$. Klages and coworkers[14] prepared some ether complexes of $HSbCl_6$ and examined their nmr and ir spectra. They showed that in the presence of excess ether, hexachloroantimonic acid forms a stable complex of the type II. Klages found that the



II

$^{+}OH\cdots O$ nmr resonance was far downfield. For example, for the diethyl ether complex, the resonance occurred at τ -6.4 ppm (984 cps). Therefore, the appearance of a proton resonance far downfield in our experiments can reasonably be associated with the formation of $HSbCl_6$. Klages' results indicate that the proton would be present in a dietherate of the type II.

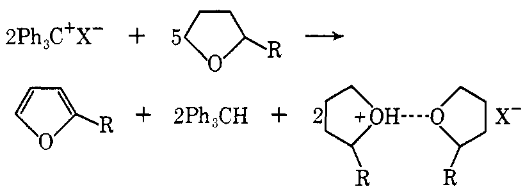
Thus the product of hydride ion abstraction, presumably I, appears to be an unstable entity. I appears to lose a proton. The net result is a dehydrogenation reaction.

Dehydrogenation of tetrahydrofurans should, of course, lead to dihydrofurans and furans. In one case, Figure 3, we obtained evidence for the presence of a furanic proton. However, most of the furanic products produced would be expected to resinify under the strongly acidic conditions.[15] They produce highly colored polymers which have never been characterized. The resulting resins, even though apparently soluble, might give highly split nmr absorptions and so would be difficult to detect in the low concentration in which they would be found above. Reaction with furans would consume some of the acid formed. This might explain in part the poor efficiency sometimes observed in initiation with trityl salts.[5c] The formation of these products would also serve to explain the intense dark brown color which invariably appeared in the nmr tubes upon reaction of Ph_3CSbCl_6 with 2-MeTHF or THF.

Polymerizations of THF catalyzed by trityl salts are characterized by dark colors. We know that dark colors are not characteristic of the growing oxonium ion because THF polymerizations initiated with triethyloxonium salts are virtually colorless.

Furthermore, our data show that no acidic protons were formed in the reaction of a triethyloxonium salt with 2-MeTHF. The only reaction occurring seems to be that shown in eq 4. This shows that the acidic proton is not a function of the polymerization process, or a side reaction of the oxonium salts. Rather it is characteristic of the initiation process occurring with trityl salts.

The above discussion suggests the reaction of trityl salts with 2-MeTHF or THF is represented by either eq 5 or 6. In both equations, R = H or Me. In



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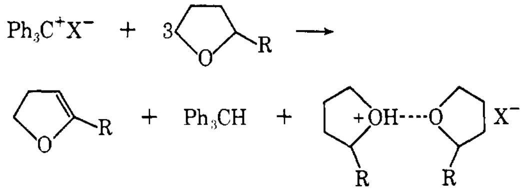

(6)

either case more than 1 mol of the THF is required The acid formed protonates a THF molecule, and probably complexes with another THF molecule. This may render at least one of them unreactive toward reaction with the trityl salt and explains why more than 1 mol of THF is required to react with 1 mol of trityl salt.

Note that if eq 6 is followed, 1 mol of THF is consumed per mole of trityl salt charged. Hence the expected ratio of RTHF to Ph_3CH in the completed reaction should correspond to (RTHF $-$ Ph_3C^+)/Ph_3C^+ (column 6, Table I). On the other hand if eq 5 is followed, only 0.5 mol of THF is consumed per mole of trityl salt charged. And the expected ratio of RTHF to Ph_3CH should correspond to (RTHF $-$ $^1/_2Ph_3C^+1$) (column 5, Table I).

A two-step ionic dehydrogenation by trityl salts has been proposed before. In 1959, Bonthrone and Reid[16] reported the dehydrogenation of a number of hydrocarbons, ketones, and heterocycles with triphenylmethyl perchlorate. They proposed a two-step process —hydride ion transfer to the trityl cation followed by loss of a proton. If the intermediate carbonium ion

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(11) H. Meerwein, V. Hederich, H. Morschel, and K. Wunderlich, *Ann.*, **635**, 1 (1960).

(12) M. Gomberg, *J. Amer. Chem. Soc.*, **35**, 200 (1913).

(13) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *ibid.*, **79**, 4557 (1957).

(14) F. Klages, J. E. Gordon, and H. A. Jung, *Chem. Ber.*, **98**, 3748 (1965).

(15) A. P. Dunlop and F. N. Peters, "The Furans," Reinhold Publishing Corp., New York, N. Y., 1953, pp 47, 64, 65.

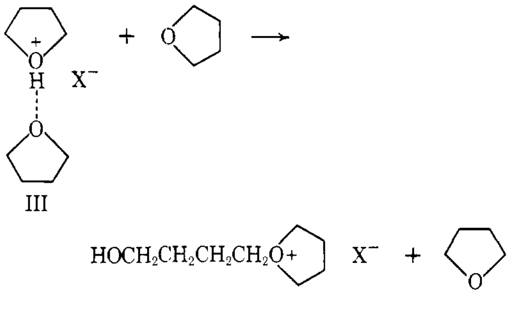
(16) W. Bonthrone and D. H. Reid, *J. Chem. Soc.*, 2773 (1959).

was sufficiently stable, as it was in the case of the perinaphthenylium ion, the reaction stopped at that stage. This is also the case in the above-mentioned reaction of trityl salts with cycloheptatriene.[13] The proton was not lost and the new ionic salt was isolated. But generally dehydrogenation occurred. The compounds which were reported to dehydrogenate include 9,10-dihydroanthracene, perinaphthan-1-one and 5,10-dihydroindolo[2,3-*a*]indene. They report one case, namely, reaction of Ph_3CClO_4 with 4,5:9,10-tetrahydropyrene, where only the doubly dehydrogenated product and starting material were isolated even when the tetrahydropyrene was in excess.

Clearly the dehydrogenation of 2-MeTHF by Ph_3CClO_4 is analogous to the reaction reported by Bonthrone and Reid. All trityl salts we investigated seemed to react similarly. Whereas most cases investigated by Bonthrone and Reid resulted in the loss of 1 mol of hydrogen and only one led to the loss of 2 mol of hydrogen, the present situation is variable. The data in Table I show that, depending on the gegenion and on the substitution on the THF ring, 1 or 2 mol of hydrogen may be extracted. This can be seen by comparing column 3 with column 5 and 6 in Table I. In some cases, notably the experiment with Ph_3CClO_4, the results are between the loss of 1 and 2 mol of hydrogen and apparently both furans and dihydrofurans were formed. However, we do not have enough data at this time to define the nature of the effect of gegenion or of ring substitution on the stoichiometry of the reaction.

The reaction of trityl salts with other cyclic ethers such as trioxane or dioxolane is probably just one of hydride ion abstraction. A stable cation is formed and a β-proton is not available for the second step to occur.

We have seen in eq 5 and 6 that the reaction of trityl salt with THF leads to a protonic acid probably complexed with two molecules of THF. This is a dialkyloxonium ion and is not yet the trialkyloxonium ion required for polymerization. We propose that the reaction leading to the required trialkyloxonium ion in catalysis of THF polymerization with trityl salts is eq 7. There is evidence that the dialkyloxonium ion



(7)

III is less reactive than the trialkyloxonium ion.[17]

The apparent formation of a stable diether complex[14] may be in large measure responsible for this. Thus although the reaction of the trityl salt with THF to form the acid initiator is indeed a fast reaction, the initiation reaction itself may be relatively slow. The proposed initiation reaction leads to hydroxyl end groups. These hydroxyl end groups may react with active sites to regenerate a dialkyloxonium ion complex. If this occurs, the apparent propagation reaction would also be slowed.

One would not expect to see hydroxyl end groups as a separate peak in the nmr spectrum. Since the dialkyloxonium ion complex seems to be rather stable, some of these species may persist throughout the polymerization. If there are protons on a positive oxygen, these and the protons on the hydroxyl end groups would be expected to undergo rapid exchange. Hence the nmr spectrum should show only one peak. The persistence and shifting of the far downfield peak in the nmr spectrum even after 5 hr of polymerization and 45% conversion to polymer is thus not surprising.

Initiation with $4\text{-}ClC_6H_4N_2PF_6$ also seems to proceed by a similar mechanism. Meerwein[18] has reported dehydrogenation reactions using diazonium salts as hydrogen acceptors. We have reported previously[19] that $4\text{-}ClC_6H_4N_2PF_6$ reacts with THF to abstract a proton. The nmr experiment reported here confirms this and shows that this too is followed by the appearance of a greatly deshielded proton in the spectrum. Polymerizations initiated by this diazonium salt are also characterized by dark colors, once again suggestive of the formation of furans.

Conclusions

The reaction of trityl salts with THF is a dehydrogenation reaction leading to Ph_3CH, a protonic acid, and furan or dihydrofuran. The acid, complexed with monomer, is the true polymerization initiator. Consequently, the polymer formed should have hydroxyl end groups on at least one end. A similar reaction probably also occurs when diazonium salts react with THF.

Trityl and diazonium salts remain convenient initiators to use for THF polymerization. But the over-all initiation process is complex. It may be slow and the number of active sites produced is not known. Also, colored polymers are formed. For theoretical studies where an exact knowledge of the number of growing centers is desired, preformed trialkyloxonium salt should be used.

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(17) J. B. Rose, *J. Chem. Soc.*, 542, 546 (1956).

(18) H. Meerwein, K. Wunderlich, K. F. Senner, *Angew. Chem. Intern. Ed. Engl.*, **1**, 613 (1962); H. Meerwein, H. Allendörfer, P. Beekmann, F. Kunert, H. Morschel, F. Pawellek, and K. Wunderlich, *Angew. Chem.*, **70**, 211 (1958).

(19) M. P. Dreyfuss and P. Dreyfuss, *J. Polym. Sci., Part A-1*, **4**, 2179 (1966).