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Initiation of cationic polymerization by tetramethylene zwitterions from tetracyanocyclobutanes

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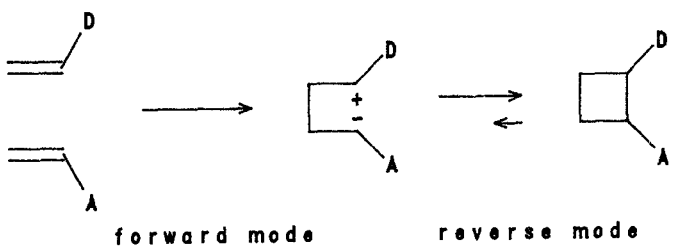
ABSTRACT

The initiating ability of tetramethylene zwitterions formed from cyclobutane adducts of donor olefins with TCNE was investigated. Polar solvents increased the ability of vinyl ether-TCNE cyclobutane adducts to initiate the cationic polymerization of N-vinylcarbazole. The concept of charge separation in the tetramethylene zwitterions was also investigated.

INTRODUCTION

Huisgen and his colleagues demonstrated zwitterion intermediates in the cycloaddition of electron-rich olefins to tetracyanoethylene TCNE.[1,2] We showed that analogous zwitterions from more reactive olefins could initiate the cationic polymerization of the olefins in certain cases.[3-5] These polymerizations were limited to the very electron-rich, easily cationically polymerized N-vinylcarbazole and N-ethyl-3-vinylcarbazole,[6] and to ketene acetals.[7]



D - donor substituent(s)

A - acceptor substituent(s)

Although vinyl ethers are known to polymerize cationically under the influence of strong Lewis acids such as boron trifluoride, neither we nor Huisgen have observed their polymerization by TCNE. Stille was able to show that the tricyanoethenol impurity present in ordinary TCNE accounted for its apparent ability to polymerize vinyl ethers.[8] The Coulombic attraction and close proximity of the initiating carbocation and the carbanionic counterion in a zwitterionic tetramethylene is one of the main reasons why most zwitterions prefer to close to form the cyclobutane adduct.

However, the reactivity of a zwitterionic tetramethylene could be enhanced by the polarity of the solvent, as already shown by the study of the initiating ability of the cyclobutane adduct of N-vinylcarbazole and dimethyl 1,1-dicyanoethylene-2,2-dicarboxylate.[3]

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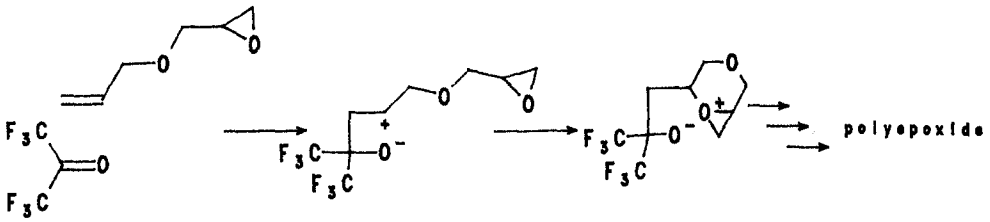
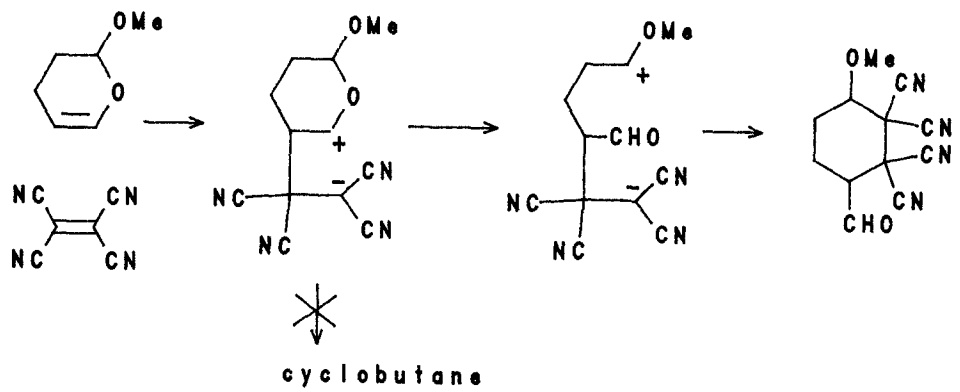
In a second concept for increasing zwitterion initiating ability, the cationic and anionic charges in the zwitterion might be separated. Adelman found polymerization of allyl glycidyl ether in the presence of hexafluoroacetone.[9] He postulated the formation of a 1,4-zwitterionic intermediate, which can isomerize to an oxonium ion. The oxonium ion is farther removed from the carbanion and is able to initiate the cationic polymerization of the excess allyl glycidyl ether.



In another instance of this concept, Williams observed an unusual reaction of 3,4-dihydro-2-methoxypyran with TCNE. No cyclobutane was formed, but a compound containing an aldehyde function.[10] He proposed the following reaction involving a charge separation of the zwitterion.



In this paper we shall explore the possibilities for better cationic initiation in the donor olefin - TCNE systems.

(1) The use of excess monomer and polar solvent to enhance the polymerization of a typical vinyl ether, isobutyl vinyl ether (IBVE), initiated by its zwitterion with TCNE, will be investigated. The zwitterion can be generated either directly from the components (forward reaction), but preferably from their cyclobutane cycloadduct (reverse reaction).

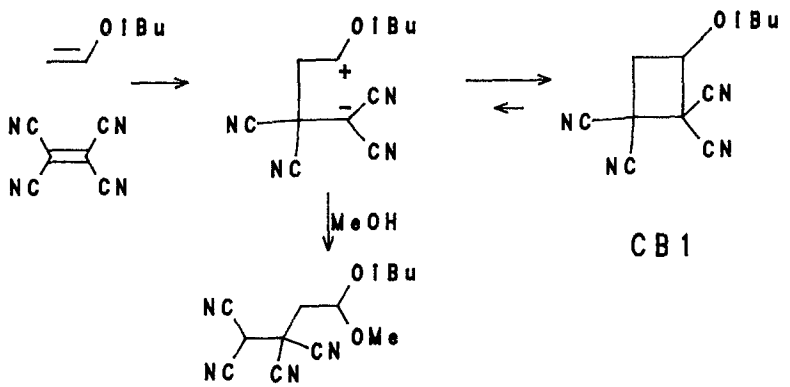
(2) Using vinyl glycidyl ether (VGE), an attempt will be made to separate the ionic charges in the zwitterion with TCNE to a new, more effectively initiating, isomeric zwitterion. Again the zwitterion will be generated in both the forward and reverse mode.

(3) A second attempt to separate the ionic charges will be made to enhance cationic initiating ability in the case of the zwitterion for 2-ethoxydihydropyran and TCNE, in which case only the forward mode is available.

RESULTS

IBVE and TCNE

The cyclobutane adduct CB1 was synthesized as before[1] from the reaction of IBVE and TCNE. That this reaction proceeds via a zwitterionic intermediate, was shown previously by Huisgen by the high increase in reaction rate in more polar solvents and by trapping it with methanol[1].



In this forward reaction of IBVE and TCNE, excess IBVE or an added monomer 1,3-dioxepane did not polymerize during the cycloaddition. Control experiments show that TCNE can initiate the cationic homopolymerization of N-vinylcarbazole (NVCZ)[5] as shown in Table 1.

Because CB1 can be isolated and purified, its initiating ability for the polymerization of reactive monomers could be investigated. In this study we used NVCZ, excess IBVE, 1,3-dioxepane, and propionaldehyde.

For NVCZ, benzene or dichloromethane are not polar enough to cause ring-opening of CB1 and initiation of its cationic polymerization at room temperature. As shown in Table 1, in more polar solvents such as acetonitrile and nitromethane, polymer was obtained in about 20% yield. The highest yield and MW for poly-NVCZ initiated by CB1 was obtained in sulfolane. Curiously nitrobenzene was ineffective in this case.

Using CB1 in excess IBVE in acetonitrile, a conversion to 5% IBVE polymer could be observed after 4 days at room temperature. The yield was increased by changing the solvent.

CB1 can initiate the cyclotrimerization of propionaldehyde in bulk. That ability was also mentioned by Huisgen during the cycloaddition of TCNE and ethyl vinyl ether,[11] and in one of our earlier papers for TCNE and some trisubstituted acceptor olefins.[6] (Polymerization beyond oligomers does not occur due to the low ceiling temperature of this aldehyde.)

Vinyl Glycidyl Ether VGE and TCNE

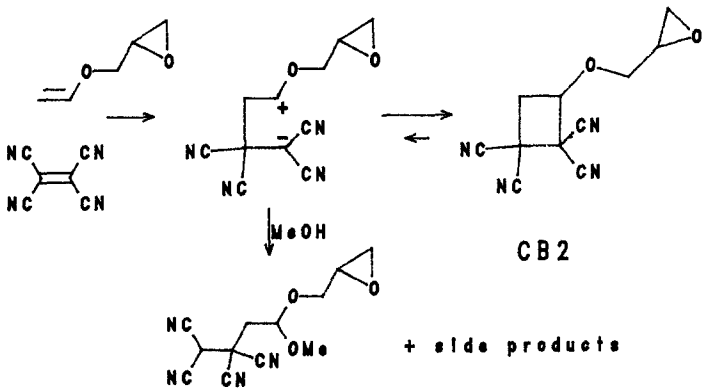
VGE reacts with TCNE in 1 to 1 molar ratio in dichloromethane to the corresponding cyclobutane CB2. A yellow charge transfer complex was observed, which did not vanish after one day. On workup at that time, the yield after purification was 61%. NMR analysis shows the presence of two diastereomers due to the two asymmetric carbons in CB2.

Table 1: Polymerization of NVCZ by Cyclonitanes in Different Solvents

Initiator	Solvent	Time	Yield of Polymer	Mn	MWD
Control Experiments					
TCNE	acetonitrile	16 hrs	25%	21900	2.3
TCNE	nitrobenzene	16 hrs	69%	95200	1.2
TCNE	sulfolane	16 hrs	76%	147400	1.02
CB1	benzene	4 days	trace	---	---
CB1	dichloro-methane	4 days	1%	---	---
CB1	acetonitrile	16 hrs	20%	29000	1.6
CB1	nitroethane	16 hrs	16%	11000	1.7
CB1	nitrobenzene	16 hrs	trace	--	---
CB1	sulfolane	16 hrs	88%	136600	1.1
CB2	acetonitrile	3 days	6%	27400	1.6
CB2	acetonitrile/ nitroethane (1:1)	3 days	2%	11900	1.3
CB2	nitrobenzene	16 hrs	40%	140000	1.1
CB2	sulfolane	16 hrs	50%	96600	1.2

a. [initiator] = 0.25 mmole, [NVCZ] = 2.5 mmole, 4 ml solvent, 28°C.

The fact that the zwitterionic intermediate can be formed from CB2 was demonstrated by trapping it with methanol under controlled conditions in deuterated chloroform with about five equivalents of methanol. Longer reaction times led to subsequent ring-opening of the epoxide.



In the forward reaction, starting from the olefins, excess VGE or 1,3-dioxepane did not polymerize during the cycloaddition. In the reverse direction, the isolated CB2 was able to initiate the cationic polymerization of NVCZ, as shown in Table 1. Again the polarity of the solvent played an important role. CB2 was not able to initiate the polymerization of IBVE, even in very polar solvents such as nitromethane. Mixing CB2 with excess propionaldehyde initially leads to trimerization of the latter, but in contrast to the reaction with CB1, higher oligomers form after longer reaction times, probably due to side reactions involving the epoxide group.

2-Ethoxy-3,4-dihydropyran (EDP) and TCNE

We used the ethoxy derivative instead of 2-methoxy-3,4-dihydropyran used by Williams,[10] because the former is more readily available. EDP and TCNE reacted readily through a red charge transfer complex, but a mixture of products resulted. The mixture of products showed the presence of an aldehyde function in the NMR and IR spectra, in agreement with Williams' results. Despite several attempts, we were unable to isolate a cyclobutane adduct by changing solvents or by running the reaction at low temperature. In the presence of IBVE or 1,3-dioxepane, the same mixture of cycloadducts was obtained, and no polymer formed.

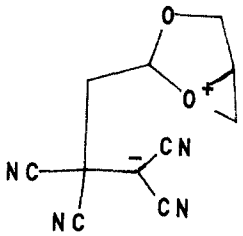
DISCUSSION

We have demonstrated weak initiating ability of cyclobutane cycloadducts as precursors of tetramethylene zwitterions. They are able to polymerize more reactive donor olefins, which could not be studied in the forward mode because cycloadditions compete successfully with initiation.

Highly polar solvents help the opening of the CB ring and also raise the propagation rate. There is also a notable solvent specificity about this process, as shown in the variable effectiveness of nitrobenzene between CB1 and CB2. Specific solution effects are currently under study in several laboratories[12,13] and more progress can be expected.

We tried to apply the Adelman concept of charge separation but without success as yet. To increase olefin donor strength, we used vinyl glycidyl ether in place of his allyl ether. The cyclobutane adduct of VGE and TCNE,

CB2, behaved exactly analogously to CB1 and no effects ascribable to internal charge separation were found. Perhaps the bicyclo[3.1.0]hexyl structure of the putative oxonium ion is too strained.



Inconclusive results were obtained in the 2-ethoxypyran work largely because we were unable to isolate the cyclobutane cycloadduct. We confirmed Williams' results and support his proposed mechanism.

EXPERIMENTAL

Instrumentation:

For NMR measurements a WM 250 FT-NMR Bruker spectrometer was used. The IR measurements were done with a Perkin Elmer IR spectrophotometer Model 983. The molecular weights were determined by Size Exclusion Chromatography (SEC) in chloroform using polystyrene as standards. The column was Phenogel 10^3. The elemental analysis was done by Desert Analytics, Tucson.

Chemicals:

N-Vinylcarbazole (NVZ) (Pfaltz & Bauer) was recrystallized from hexane. i-Butyl vinyl ether (IBVE) (Aldrich) was fractionally distilled and stored under argon over molecular sieves in the freezer. Propionaldehyde (Aldrich) was dried over magnesium sulfate, fractionably distilled in the presence of hydroquinone and kept under argon. 3,4-Dihydro-2-ethoxypyran (Pfaltz & Bauer) was fractionallly distilled. 1,3-Dioxepane was prepared according to the literature[14] and twice fractionally distilled from calcium hydride. Tetracyanoethylene (TCNE) (Aldrich) was sublimed twice through charcoal and recrystallized from dichloroethylene.

Acetonitrile and sulfolane were dried over magnesium sulfate and distilled from calcium hydride. Nitrobenzene was distilled from magnesium sulfate, phosphorus pentoxide, and barium oxide. Nitromethane was dried over calcium chloride and fractionally distilled. Dichloromethane was extracted with concentrated sulfuric acid and sodium carbonate aqueous solution, dried over magnesium sulfate and distilled from calcium hydride.

Vinyl Glycidyl Ether:

The vinyl glycidyl ether was prepared following patent literature.[15,16] 1-Chloro-2-hydroxyethane (143.5g, 1.78 mole) and 82.3g (0.89 mole) epichlorohydrin were stirred in the presence of 1 ml conc. sulfuric acid at 125°C for 20 hrs. The product, 1-chloro-2-hydroxy-3(2-chloroethyl)propyl ether was distilled under vacuum at 65-75°C. To 50.6g (0.29 mole) of the latter, 10.8g (0.27 mole) sodium hydroxide and 100 ml water were added. The mixture was stirred 1 h at room temperature and 1 h at 100°C. By distillation at high vacuum 69 % of 1-chloroethyl-2-glycidyl ether could be obtained. To 28.7g (0.21 mole) of the ether, 8g (0.20 mole) sodium hydroxide and 60 ml diglyme were added and the mixture was stirred for 3 h at 140° C. The vinyl glycidyl ether could be separated from this mixture by several fractional distillations

over a glass packed column. Overall yield: 10 %, bp. 128-129°C (0.5 torr) NMR ($CDCl_3$):2.68 (dd, 1H), 2.85 (dd,1H), 3.25 (m,1H), 3.62 (dd,1H), 3.9-4.1 (2 dd,2H), 4.23 (dd,1H), 6.48 (dd,1H) ppm. IR (KBr): 1640,1620 (=CH), 1200 (epoxide) cm^{-1}

1,1,2,2-Tetracyano-3-i-butoxycyclobutane (CB1)
The cyclobutane was prepared as described before[6]. The solvent in this case was methylene chloride. The product could be recrystallized from methylene chloride/hexane (1:20).

1,1,2,2-Tetracyano-3-glycidoxycyclobutane (CB2):
TCNE (1.28g, 0.01 mole) was dissolved in 60 ml dichloromethane and 1.0g (0.01 mole) vinyl glycidyl ether was added. The solution was stirred for 20 h at room temperature. TCNE forms a yellow CT-complex with the vinyl ether. The product could be isolated by adding hexane to the reaction mixture. The cyclobutane was recrystallized twice from methylene chloride/hexane (1:20). Yield: 61 %, white crystals, mp. 90-92°C. In the NMR two sets of signals were found indicating two diastereomers.
NMR ($CDCl_3$): set 1: δ 2.72 (dd,1H), 2.93 (t,1H), 3.16 (t,1H),3.275 (m,1H), 3.40 (dd,1H), 3.56 (dd,1H), 4.28 (dd,1H), 4.79 (dd,1H) ppm: set 2: δ 2.77 (dd,1H), 2.91 (t,1H), 3.18 (t,1H), 3.23 (m,1H), 3.42 (dd,1H), 3.65 (dd,1H), 4.21 (dd,1H), 4.82 (dd,1H) ppm. IR (KBr): 3030, 2936, 2252 (CHstr.), 2138 (CN), 1450, 1336, 1260, 1203, 1011, 911, 861 cm^{-1}. Elem. Anal.: calcd. C, 57.89; H, 3.50; N, 24.56; found C, 57.64; H, 3.44; N, 23.50.

Polymerization Procedure using NVCZ as the Monomer:
NVCZ (2.5 mmole) was dissolved in 4 ml solvent in a dry polymerization tube. The solution was degassed twice. The initiating compound (.25 mmole) was dissolved in 1 ml of the solvent under argon and added to the monomer solution by syringe. The reaction mixture was stirred at room temperature. In sulfolane it was necessary to increase the temperature to 40°C. The polymer was precipitated in methanol. In acetonitrile and nitromethane, the reaction mixture became heterogeneous after some time because the formed polymer was not soluble in these solvents.
The same procedure was used for 1,3-dioxepane.

Polymerization Procedure using IBVE as the Monomer:
The initiating compound (0.25 mmole) was dissolved in 2 or 5 ml solvent and the solution was degassed twice. The IBVE (2,5 or 5 mmole) was added by syringe. The mixture was stirred at room temperature. To stop the polymerization, one drop of methanol was added. The solvent and unreacted monomer were removed in vacuum. The residue was checked by NMR.

Reaction with Propionaldehyde:
The cyclobutane (.42 mmole) was dissolved in 1mmole propionaldehyde and stirred under argon for 18 hrs. The trimer (2,4,6-triethyltrioxane) was isolated from the mixture by distillation and was checked by NMR. NMR($CDCl_3$) trimer: 1.0 (t,9H), 1.6 (m,6H), 4.8 (t,3H) ppm.

Reaction of TCNE and 2-Ethoxy-3,4-Dihydropyran:
TCNE (1 mmole) was dissolved in 10 ml methylene chloride and 1 mmole of the pyran was added. The color of the solution turns red, indicating a CT-complex. After 7 h at room temperature the solution was almost colorless. White crystals could be isolated by adding hexane. Yield: 57%. The product showed

the aldehyde functionality in the IR (1730 cm^{-1}) and the NMR (9.7ppm) spectra. At 0°C the reaction was slower. After 3 days only 20% of the TCNE has reacted.

Attempted Polymerization with 2-Ethoxy-3,4-Dihydropyran:
TCNE (1 mmole) and the pyran were dissolved in 5 ml acetonitrile or methylene chloride under argon. IBVE or 1,3-dioxepane (10 mmole) were added by syringe. The mixture was stirred at room temperature for 4 to 12 days. No polymerization occurred.

Reaction of the Cyclobutanes with Methanol:
CB1 or CB2 (.5 mmole) was dissolved in methanol. The solution was stirred for 5 hrs, then the solvent was removed, the residue dried, and checked by NMR. The reaction of CB2 with methanol was also followed by NMR. CB2 (0.2 mmole) was dissolved in $CDCl_3$ and 1 mmole methanol was added. The reaction was followed over 24 hrs.

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