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SHORT COMMUNICATION

Studies on the Polymerization of Acrolein Oxime. X. Formation and Structure Determination of a Cyclic Trimer from Methacrolein Oxime

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In our previous papers,[1,2] the following conclusions were made on the thermal polymerization of acrolein oxime (AOM): (1) the reaction follows an anionic mechanism, (2) the initiating species is an anion, $CH_2=CH-CH=N-O^{\ominus}$, produced by the ionic dissociation of the molecular aggregates of AOM, and (3) the polymer obtained has a molecular weight of *ca.* 2000 and consists of two or more types of structural units, *i.e.*, 1,2-addition, 1,4-addition, and hydrogen transfer. AOM is also polymerized in the presence of a cationic or anionic catalyst.[3,4] However, AOM does not polymerize radically since it serves as an inhibitor for radical polymerizations of vinyl compounds due to the stability of the resulting iminoxy radical.[5]

Methacrolein oxime (MAOM), a substituted AOM, also undergoes spontaneous polymerization on heating to give, though very low in yield, the oligomer. This paper describes the formation and structural determination of the cyclic trimer formed as the main product in the MAOM oligomerization.

EXPERIMENTAL

Methacrolein was prepared by the Mannich reaction of propionaldehyde and formaldehyde,[6] and then oximated according to the procedure of Mowry.[7] The yield of MAOM based on methacrolein was 52%. bp 85°C [17 mmHg (2.3 kPa), n_D^{25} 1.482, d_4^{20} 0.9465.

Oligomerization was carried out in an ampoule. After the given time of reaction, the unreacted monomer was removed by a stream of nitrogen under reduced pressure, and then the residue was brought subjected to large amount of ether so that the oligomer was thus precipitated. *Anal.* Calcd for $(C_4H_7NO)_n$: C, 56.45%; H, 8.27%; N, 16.46%. Found: C, 56.05%; H, 8.28%; N, 15.74%. Upon recrystallization of the oligomer from methanol, a cyclic trimer precipitated as needle-like crystals (100 mg of the oligomer was recrystallized to give 66 mg of the crystals): mp >210°C, *Anal.* Calcd for $(C_4H_7NO)_3$: C, 56.45%; H, 8.27%; N, 16.46%. Found: C, 56.26%; H, 8.48%; N, 16.20%. ^{1}H NMR (DMSO-d_6 ppm from TMS) δ 10.71, 10.62 ($-OH$); 7.18, 7.36 ($-CH=N-$); 0.8—2.5 (multiplet of methine, methylene, and methyl). Mass spectrum *m/e* 255, 240, 211, etc. ^{1}H NMR spectrum revealed the absence of carbon–carbon double bonds.

The molecular weight was determined using methanol as the solvent by a vapor pressure osmometer (Hitachi Perkin-Elmer, model 115). Product distribution was determined by a Hitachi HLC 635 equipped with 1.5 feet of Shodex A-802 column eluted with tetrahydrofuran. ^{13}C NMR spectra were obtained with Hitachi R-42 FT (22.6 MHz), using DMSO-d_6 as the solvent and as the internal standard.

RESULTS AND DISCUSSION

The oligomerization data are summarized in Table

I. For example, when 10 cm^3 (9.47 g) of MAOM was heated at 80°C for 10 h, 0.045 g (0.5% conversion) of the oligomer was obtained. The number-average molecular weight was 276 (degree of polymerization = 3.2).

Table I. Thermal polymerization of MAOM

MAOM/ cm^3(g)	Benzene/ cm^3	Temp/ °C	Time/ h	Yield/ g
10 (9.47)	0	60	10	0.003
8 (7.57)	2	60	10	0.002
10 (9.47)	0	70	10	0.009
10 (9.47)	0	80	10	0.045

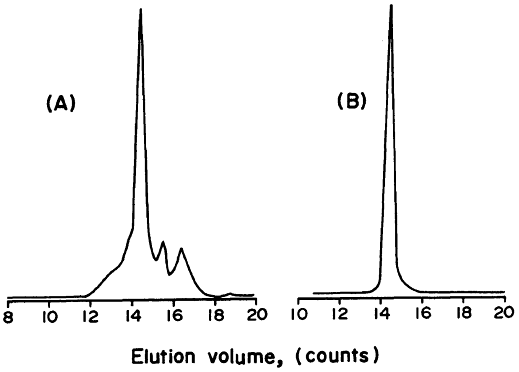


Figure 1. GPC diagrams of MAOM oligomer. (A) MAOM crude oligomer, (B) following recrystallization.

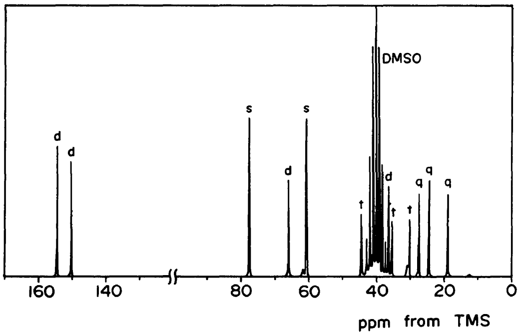
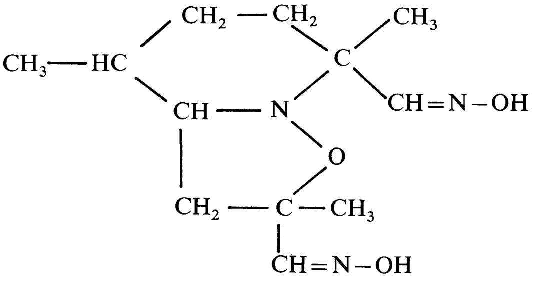


Figure 2. ^{13}C NMR spectrum of cyclic trimer (2,4,7-trimethyl perhydroisoxazo[2,3-a]pyridine-2,7-dicarbaldoxime).

Table II. Assignment of ^{13}C NMR peaks of the trimer

Structure	Peak positon ppm (from TMS)	Structure	Peak position ppm (from TMS)
	18.79	$-\underset{\vert}{\overset{\vert}{C}}H$	36.44
$-CH_3$	24.42	$-\underset{\vert}{\overset{\vert}{C}}-N$	60.75
	27.42	$-\underset{\vert}{\overset{\vert}{C}}-O$	77.62
	30.16	$>CH-N$	65.99
$>CH_2$	35.28	$-CH=N-$	150.40
	44.41		155.44

Figure 1 (A) shows a typical GPC diagram, which shows that the product has a relatively narrow molecular weight range. The component eluted at 16.5 counts is the MAOM monomer. Upon recrystallization of the oligomer from methanol, needle-like crystals precipitated. As can be seen from Figure 1 (B), these consist of one component which coincides, in the GPC peak positon, with that of the main product. Figure 2 shows ^{13}C NMR spectrum of the crystals. The crystals are made up of twelve carbons and have a molecular weight of 255 (from the results of MS measurement), *i.e.*, they are the trimer. Table II shows the assignment of ^{13}C NMR peaks of the crystals by using the off-resonance technique. These spectral data indicate that the trimer structure is 2,4,7-trimethyl perhydroisoxazo[2,3-a]pyridine-2,7-dicarbaldoxime (I).



I

To determine the crystal structure of **I**, X-ray intensities were measured on a Syntex R_3 automated four-circle diffractometer with graphite-monochromated Mo-$K_\alpha$radiation. The crystallographic data obtained are summarized in Table III, with the final value of R being 0.068. Bond lengths a[illegible] [illegible]wn

Table III. Crystal data on I

Chemical formula	$C_{12}H_{21}N_3O_3$		
Molecular weight	255.32		
Crystal system	monoclinic		
Space groups	$P2_1/a$		
Systematic absence	$h01$ $h=2n+1$, $0k0$ $k=2n+1$		
$a=7.858$	(3)Å	$Z=4$	
$b=13.186$	(6)Å	$D_x=1.243\,\mathrm{g\,cm^{-3}}$	
$c=17.259$	(6)Å	$D_m=1.239\,\mathrm{g\,cm^{-3}}$	
$\beta=130.38$	(3)Å		
$U=1362\,\mathrm{A}^3$			

in Figure 3. Further details will be reported elsewhere.

Similar to the case of AOM, the presence of azobisisobutyronitrile (1×10^{-2} mol dm^{-3}) did not affect the velocity of the bulk polymerization (60°C) of MAOM, and the thermal copolymerization of MAOM and acrylonitrile gave copolymer containing acrylonitrile unit less than 50 mol%. Further, MAOM is an efficient retarder of radical polymerization of vinyl compounds. These facts suggest that the thermal polymerization of MAOM follows an anionic mechanism.

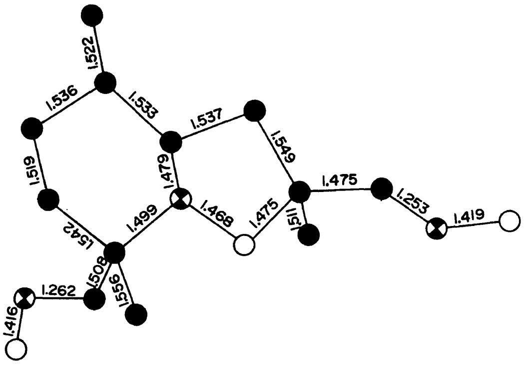
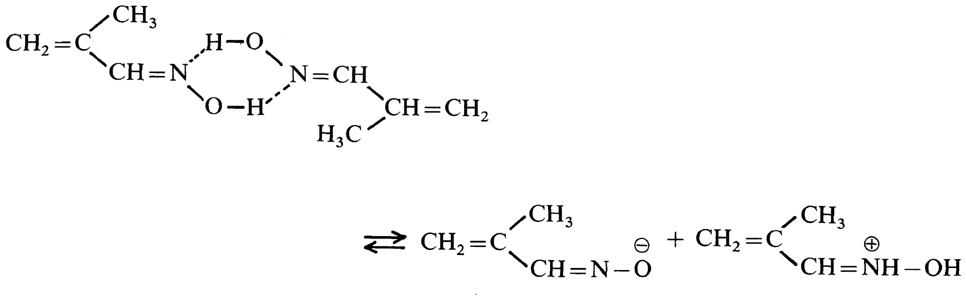


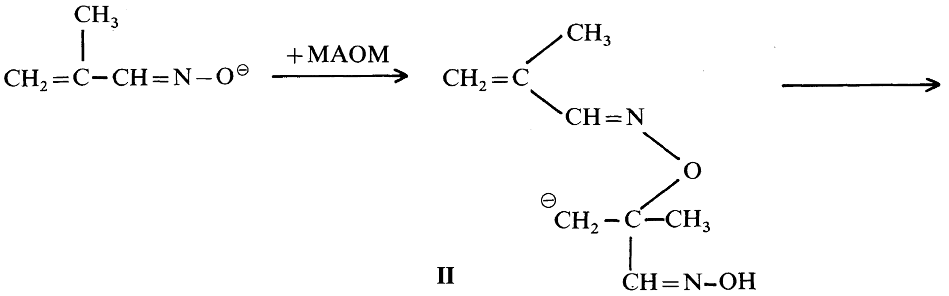
Figure 3. Bond lengths (Å) of cyclic trimer (2,4,7-trimethyl perhydroisoxazo[2,3-a]pyridine-2,7-dicarbaldoxime).
●, carbon; ⊗, nitrogen; ○, oxygen

The apparent molecular weight of MAOM in benzene at a concentration of 0.239 mol dm^{-3} was cryoscopically determined as 140, and this gives an estimate of 1.65 for the aggregation factor. Thus, MAOM in liquid is in the aggregated form as well as many other oximes.[8] The initiating species is the MAOM anion (MAOM$^\ominus$), arising from the dissociation of the molecular aggregates of the oxime.

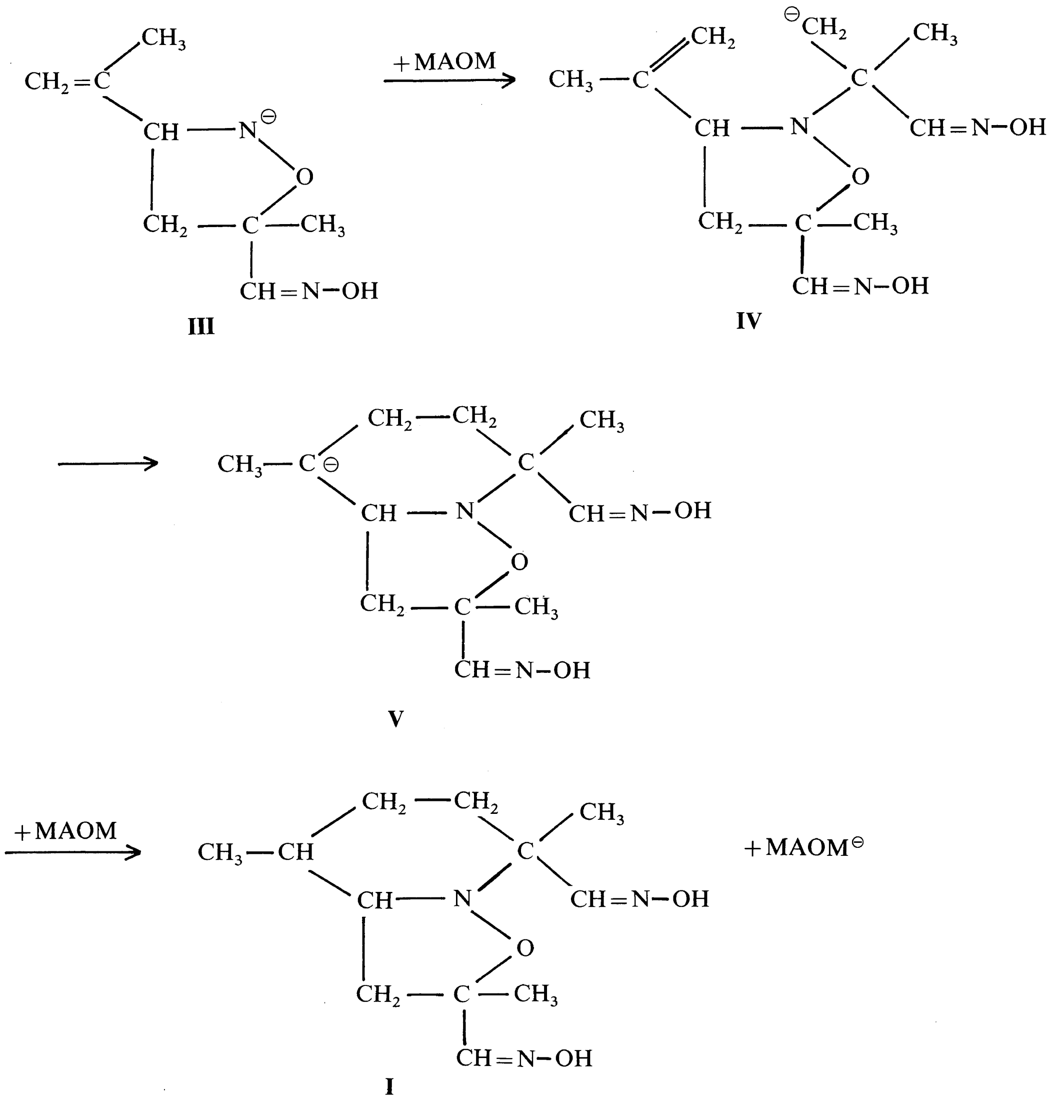


(MAOM$^\ominus$)

Thus, the oligomerization processes may be represented as follows.



II



III

IV

V

I

Head-addition is operative in the thermal polymerization of AOM, whereas BuLi induces tail-addition to the vinyl group and addition to the oxime group, other than head-addition, in an equimolar reaction with AOM, particularly without solvent.[9] The tail-addition may be predominant in the oligomerization of MAOM due to high electron density of a β-carbon, which may be attributed to the electron-donating property of methyl group.

When intermediate **II** is propagated and cyclized, a linear oligomer and intermediate **III** are formed, respectively. The addition of MAOM to **III** leads to intermediate **IV**. A large portion of **IV** is converted into the cyclic trimer **I** through intermediate **V** though further addition of MAOM may be possible. The GPC diagram (Figure 1(A)) shows the dimer, trimer, tetramer, and so on. On the other hand, several compounds, two of which having molecular weights of 170 (from the results of GC-MS measurement), were found also in the ether solution from which the oligomer precipitated had been removed by filtration. The structures of oligomers other than the cyclic trimer are being investigated at present and will be presented elsewhere.

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