

Epoxidation of cyclic olefins using dimeric molybdenum(VI) catalysts

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Abstract

Catalytic properties of dimeric molybdenum(VI) triketonates were compared to those of $\text{MoO}_2(\text{acac})_2$ in the epoxidation reaction of cyclooctene and 1,5-cyclooctadiene with tertiary butyl hydroperoxide. Studies of the reaction at a molar ratio of olefin:TBHP:catalyst = 1:1:0.001 for the monoolefin and 1:2:0.001 for the diolefin at 40 and 80 °C in dichloroethane were carried out. The dimeric Mo(VI) complexes preferentially catalyzed the production of a monoepoxide.

Introduction

The direct oxidation of hydrocarbons to form epoxides has many industrial applications [1-3]. The preparation of epoxides from olefins typically requires the use of strong oxidizing agents such as hydroperoxides, hydrogen peroxide or hypochlorous acid [4]. It is well known that transition metal complexes catalyze the rapid conversion of olefins to epoxides [5]. $\text{MoO}_2(\text{acac})_2$ [6-10] and several other molybdenum compounds have been studied. These include, among others, *cis*-dioxomolybdenum(L), where L is derivatives of acetylacetonate [11], molybdenum bis(diphenylphosphine)ethane complexes of varying oxidation states [12], molybdenum(V) porphyrins [13], molybdenum hexacarbonyl [14] and molybdenum dithiocarbamates [15]. One dimeric complex, $\text{H}_2[\text{Mo}_2\text{O}_4(\text{Ox})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$, has been studied [6].

The reactions in this study were all performed using cyclic olefins and the oxidizing agent tertiary butyl hydroperoxide (TBHP) in 1,2-dichloroethane. The catalysts used were dimeric molybdenum(VI) species of the form shown in Fig. 1. The activity of the dimeric catalysts was compared to that of $\text{MoO}_2(\text{acac})_2$.

Experimental

Materials

All chemicals were purchased from Aldrich Chemical Company.

Gas chromatographic analysis was used to verify the purities of the 70% tertiary butyl hydroperoxide (azeo-

tropically dried with 1,2-dichloroethane) [4], 1,2-dichloroethane, cyclooctene and 1,5-cyclooctadiene.

Molybdenum compounds

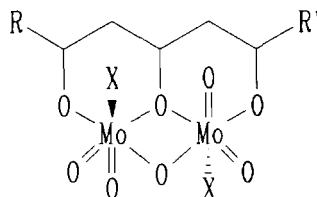
The dimeric Mo(IV) triketonates were prepared as described by Borer and Sinn [16]. A dimeric Mo(VI) complex with the ethylenediammine Schiff base derivative was prepared following the procedures of Lintvedt *et al.* [17]. The ligand (2.5 g, 3.62 mmol) was dissolved in 100 ml of ethanol. $\text{MoO}_2(\text{acac})_2$ (7.9 g, 19.1 mmol) was dissolved in 100 ml of ethanol and added to the ligand. The solution was then refluxed for 1 h. The orange solid was recovered by vacuum filtration and washed with an ethanol/water mixture. *Anal.* Calc. for $\text{C}_{26}\text{H}_{24}\text{Mo}_2\text{N}_2\text{O}_8 \cdot 2\text{C}_2\text{H}_6\text{O}$: C, 46.39; H, 4.64; N, 3.61; Mo, 24.74. Found: C, 46.63; H, 4.71; N, 3.69; Mo, 24.68%.

Instrumentation

Epoxide formation was determined with a Hewlett Packard model 5840A gas chromatograph equipped with a 30 m, SE-54, Alltech Econo-cap column, and flame ionization detector. Mass spectra were determined using a Hewlett Packard 5895 GC-MS spectrometer operating in electron impact mode, employing a 70 eV ionization potential and was equipped with a 30 m DB-5, 0.25 mm diameter capillary column. Proton NMR spectra of DCCl_3 sample solutions were determined at 60 MHz using a Perkin-Elmer R-20 spectrometer. IR spectra were collected using KBr disks in conjunction with a Perkin-Elmer model 1800 spectrometer.

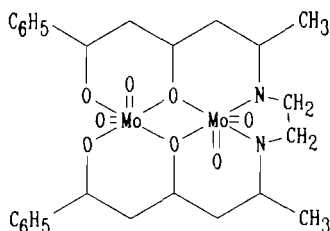
Analysis was done by Galbraith Laboratories, Knoxville, TN.

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Compound 1(a-d)

- a) (1,5-diphenyl-1,3,5-pentanetrionato)(μ -oxo)bis(dimethyl sulfoxide)dioxomolybdenum(VI)
(DBA DMSO); [R=R'=C₆H₅, x=DMSO]
- b) (5-phenyl-2,4,6-hexanetrionato)(μ -oxo)bis(ethanol)dioxomolybdenum(VI)
(BAA Et); [R=CH₃, R'=C₆H₅, x=ethanol]
- c) (1,5-diphenyl-1,3,5-pentanetrionato)(μ -oxo)bis(ethanol)dioxomolybdenum(VI)
(DBA Et); [R=R'=C₆H₅, x=ethanol]
- d) (5-phenyl-2,4,6-hexanetrionato)(μ -oxo)bis(dimethyl sulfoxide)dioxomolybdenum(VI)
(BAA DMSO); [R=CH₃, R'=C₆H₅, x=DMSO]



Compound 2

[μ -[5,5'-(1,2-ethanediyldinitrilo)bis(1-phenyl-1,3-hexanedionalo)]dioxomolybdenum(VI)
(Mo₂(BAA)₂en)

Fig. 1. Structure and nomenclature of dimeric molybdenum(VI) catalysts.

Procedure

A 100-ml three-necked round-bottom flask was charged with 1,2-dichloroethane (15 ml), cyclooctene or 1,5-cyclooctadiene (2.57 ml, 21.0 mmol) and a micro-magnetic stir bar. The flask was equipped with a thermometer, condenser fitted with a nitrogen purge, and a rubber septum to facilitate sample extraction. The reaction mixture was gradually heated until the desired temperature (40 or 80 °C) was reached. At this point, the rubber septum was briefly removed for the addition of (5 ml, 21.0 mmol for olefin or 10 ml, 41.9 mmol for diolefin) of dried tertiary butyl hydroperoxide (TBHP), and 0.025 mmol of the appropriate molybdenum catalyst. The reaction was carried out for a period of 2 h, with a sample being withdrawn every 5 min. Three drops of the withdrawn sample were placed in a 25-ml separatory funnel containing 1,2-dichloroethane (5 ml). Saturated sodium sulfite solution (1 ml) was added to the vessel to quench the epoxidation reaction. The organic layer was then removed and

transferred to a 5-ml Teflon-capped sample vial containing sodium sulfate (approximately 0.5 g) for removal of any remaining moisture. A sample (1 μ l) was then injected into the GC column for analysis.

9-Oxabicyclo[6.1.0]nonane (3) and 5,10-dioxatricyclo[7.1.0^{4,6}]decane (4)

These were identified by comparison of the GC retention time with that of authentic samples.

9-Oxabicyclo[6.1.0]nona-4-ene (5)

The monoepoxide 5 was isolated from the reaction study by flash chromatography using silica gel (230–400 mesh) and eluting with hexane. GC-MS showed a single component in the GC trace. GC-EIMS m/z (%): 124(M^+ , 0.5), 109(24), 79(70), 67(100). 60 MHz ¹H NMR: complex multiplets at δ 5.65 (2H), δ 3.2 (2H), δ 2.19 (8H) and is in agreement with the reported spectrum [18] for the monoepoxide 5.

Results and discussion

The catalytic activity of various molybdenum compounds was examined in an epoxidation reaction of cyclooctene with TBHP at a molar ratio of olefin:TBHP:catalyst of 1:1:0.001. The results are shown in Fig. 2. It is evident that MoO₂(acac)₂ produces the highest percentage of epoxide at a faster rate and with essentially no initiation period at this temperature (40 °C). The ethanol solvated DBA and BAA dimeric complexes are insoluble in dichloroethane and show

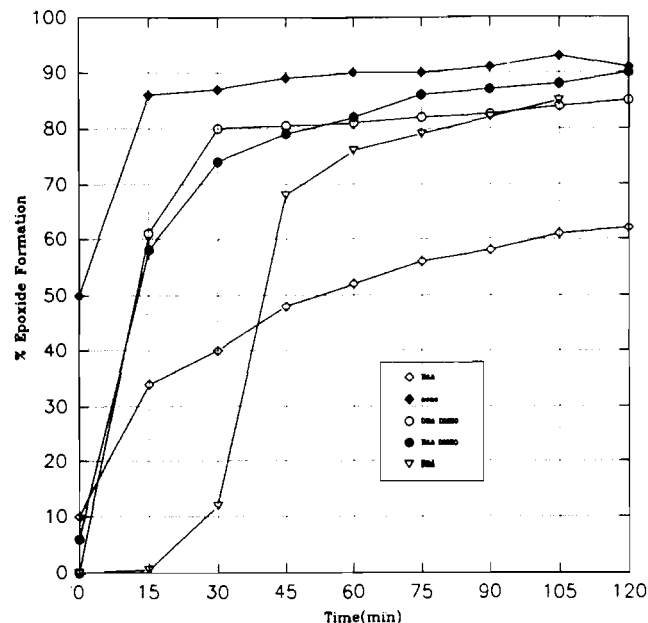


Fig. 2. Epoxide 3 formation from cyclooctene at 40 °C catalyzed by molybdenum(VI) compounds.

an extended initiation period. On the other hand, the DMSO solvated dimeric complexes are soluble in dichloroethane and catalyze the reaction more rapidly than the insoluble ethanol adducts. It is evident, therefore, that the epoxidation reaction takes place more easily in a homogeneous environment. $\text{MoO}_2(\text{acac})_2$ is more soluble in the solvent and it is well known that the ligands of $\text{MoO}_2(\text{acac})_2$ are labile [19]. An active diol intermediate has been postulated by Sharpless and Chong [20]. The dimeric complexes are not as soluble and exhibit an extended initiation period which suggests that the triketone ligand is not as labile and that the same active intermediate is not formed.

To determine the effectiveness of the dimeric catalysts with a diene, reactions using 1,5-cyclooctadiene were performed. The preferred conformation of this diene in solution is the twist-boat conformation [21] and the distance between the double bonds has been calculated at 2.6 Å [22]. The Mo-Mo distance in the DBA complex with DMSO is 3.272 Å. The *cis* MoO_2 units are *trans* to each other in this complex [16]. No crystal data is available, however it is thought that in the ethylenediamine derivative the MoO_2 units will take a similar conformation, and that the MoO_2 units will be held in a more rigid manner.

The results of the reaction of 1,5-cyclooctadiene catalyzed by $\text{MoO}_2(\text{acac})_2$ are shown in Fig. 3. There is a 1:1 ratio of monoepoxide 3 and diepoxide 4 products at 40 °C, when the ratio of olefin:TBHP:catalyst in the reaction is 1:2:0.001. This reaction can be forced to complete formation of the diepoxide 4 by either raising the temperature, adding more catalyst or more TBHP.

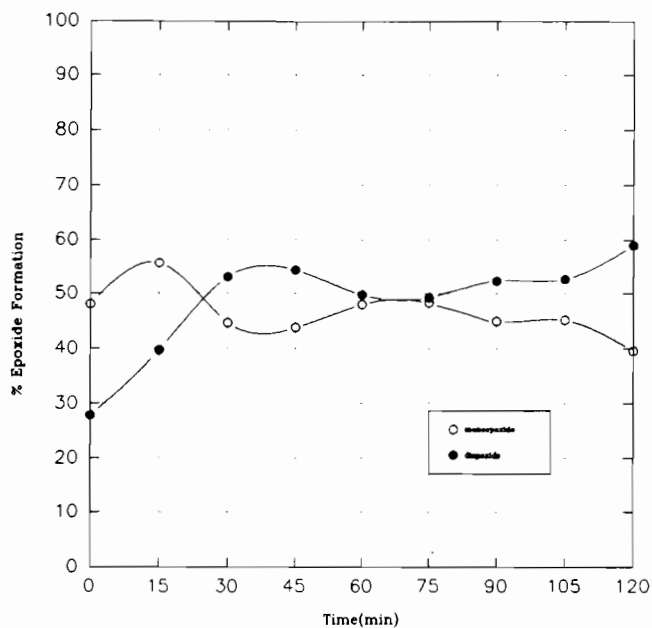


Fig. 3. Monoepoxide 5 and diepoxide 4 formation from 1,5-cyclooctadiene at 40 °C catalyzed by $\text{MoO}_2(\text{acac})_2$.

Figure 4 gives the results using the BAA DMSO complex as catalyst. The monoepoxide is preferred over the diepoxide species at 40 °C, by a ratio of 6.7:1, respectively. If the temperature is raised to 80 °C, the diepoxide will form to a greater extent as shown in Fig. 5, by a ratio of 1:1. The results of using BAA-en DMSO catalyst show a longer initiation period, however

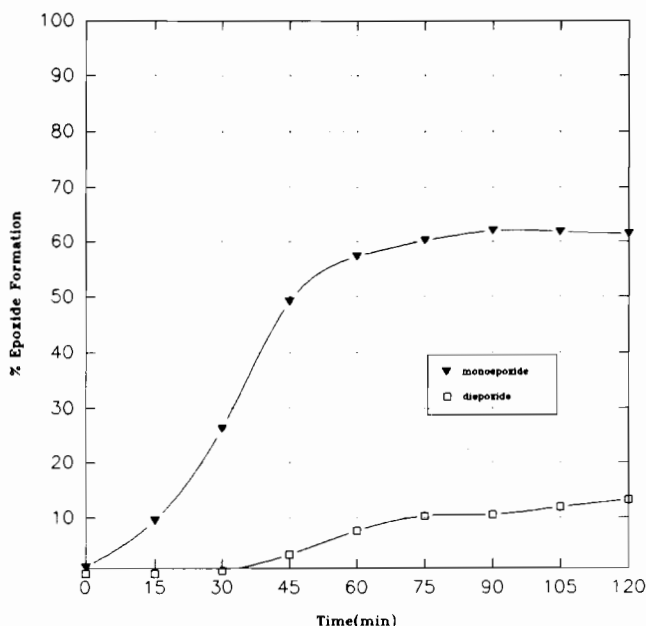


Fig. 4. Monoepoxide 5 and diepoxide 4 formation from 1,5-cyclooctadiene at 40 °C catalyzed by BAA DMSO.

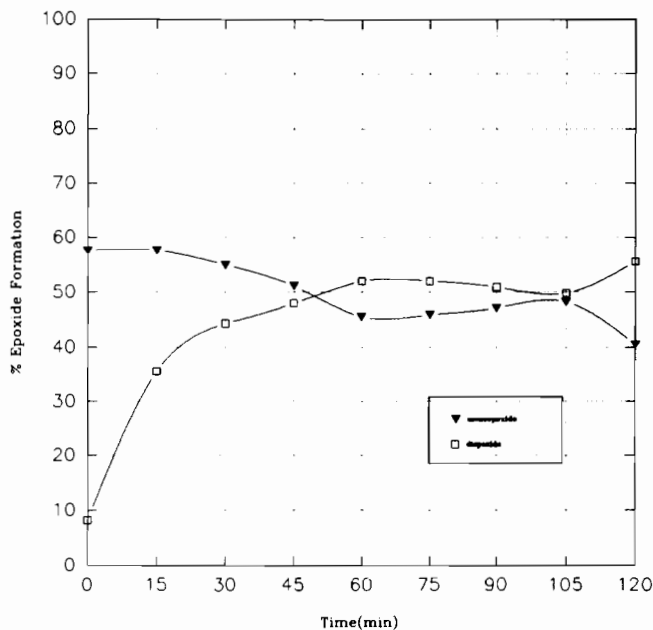


Fig. 5. Monoepoxide 5 and diepoxide 4 formation from 1,5-cyclooctadiene at 80 °C catalyzed by BAA DMSO.

after 1 h the ratio of monoepoxide to diepoxide is 6:1, similar to the results with BAA DMSO.

Electronic and steric effects have been postulated to play a role in selective epoxidation. Numerous studies have shown variations in the oxidizing ability of the MoO_2^{2+} with the ligand environment [15]. Electron withdrawing groups significantly increase the oxidizing ability. The irreversible reduction potential of $\text{MoO}_2(\text{acac})_2$ has been measured at -1.2 V [16]. The dimeric DMSO solvated BAA complex produces irreversible reduction waves at -0.9 and -1.1 V. This is consistent with the increased π -electron system in the dimeric complex. It is postulated that the diketone proceeds by a one-step reduction from the Mo(VI) to the Mo(V) species and that the triketone species proceeds by two one-electron steps. Ligand effects in the dimeric complex may be attributed to weakly activating phenyl groups and the increased reactivity of the DMSO substituents. These effects would make the oxidizing ability of the molybdenum more favorable, resulting in greater selectivity and shortening the initiation period. Differences in the reduction potentials of the two Mo centers suggest that changes occur in the molecule after the reduction of one center. It then follows that only one MoO_2 center is active in epoxidation. A sizable quantity of the monoepoxide must be formed first before the diepoxide can begin forming (Fig. 4). This suggests that the diepoxidation occurs in a stepwise fashion rather than simultaneously.

We have shown that the dimeric Mo(VI) complexes are not effected in the presence of TBHP alone. The protracted initiation period and subsequent low yield of the diepoxide species suggests that the Mo(VI) dimer is unchanged in the epoxidation reaction. Since the dimer remains intact, only one of the MoO_2 units is effectively used in catalysis. The second MoO_2 unit is *trans* to the first and it is not in a position to catalyze the other double bond of the diene. Steric hindrance will play a role in the effectiveness of the dimer to effect a second epoxidation. On the other hand, with $\text{MoO}_2(\text{acac})_2$ as catalyst, large quantities of the monoepoxide and diepoxide are formed immediately and level off at approximately an equal distribution of both epoxide species.

Studies continue with other dimeric Mo(VI) complexes, particularly those having a *cis* configuration of

MoO_2 units and with dienes in which the double bonds are in different environments.

Acknowledgements

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