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Solubilities of $MoO_2X_2L_2$ ($X = Cl, Br$; $L = OPPh_3, OPMePh_2$) in Dichloromethane and H_2O_2 (30 % (By Weight)) + H_2O Solution

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Dioxomolybdenum(VI) complexes of the type $MoO_2X_2L_2$ (X, L = Cl, $OPPh_3$ (**1**); Br, $OPPh_3$ (**2**); Cl, $OPMePh_2$ (**3**); Br, $OPMePh_2$ (**4**)) were synthesized and characterized by the melting point, elemental analysis, infrared spectroscopy (IR), and nuclear magnetic resonance (^1H NMR and ^{31}P NMR). Using a static analytical method, the solubilities of **1** to **4** were measured in dichloromethane in the temperature range from (283.16 to 310.41) K and in H_2O_2 (30 % (by weight)) + H_2O solution from (298.02 to 358.82) K, respectively. It was found that the solubilities of **1** to **4** in dichloromethane and H_2O_2 (30 % (by weight)) + H_2O solution decreased in the order **3** > **4** > **1** > **2**. The solubility data were correlated with an empirical equation.

Introduction

Epoxidation of olefins is a very outstanding transformation in organic synthesis. The use of transition metal complexes as the epoxidation catalysts is of particular interest, since they dramatically enhance the reaction yield, selectivity, and rate of epoxidation.[1−3] Dioxomolybdenum(VI) compounds containing phosphine oxides $MoO_2X_2L_2$ (X = Cl, Br; L = $OPPh_3$, $OPMePh_2$) (Figure 1) have been proven to be effective catalysts for the epoxidation of olefins using tertbutyl hydroperoxide (TBHP) or hydrogen peroxide as the source of oxygen.[4−7]

To be an epoxidation catalyst, high purity is needed. According to the literature,[5] $MoO_2X_2L_2$ (X = Cl, Br; L = $OPPh_3$, $OPMePh_2$) are prepared by the reaction of molybdic acid and the appropriate concentrated hydrohalic acid and phosphine oxide. The product is then recrystallized from dichloromethane. Knowledge of the solubilities of $MoO_2X_2L_2$ (X = Cl, Br; L = $OPPh_3$, $OPMePh_2$) in dichloromethane are important for their preparation and purification.

Furthermore, compared to TBHP, hydrogen peroxide is rather inexpensive, and it is a green oxidant[8] for various organic compounds as H_2O is the only expected byproduct. Accordingly, the application of hydrogen peroxide is undoubtedly attractive. To accomplish epoxidation of olefins using dioxomolybdenum(VI) compounds as catalysts, reliable solubility data of dioxomolybdenum(VI) compounds in hydrogen peroxide are of primary importance.

In this study, dioxomolybdenum(VI) compounds $MoO_2X_2L_2$ (X = Cl, Br; L = $OPPh_3$, $OPMePh_2$) were synthesized and characterized. The solubilities of these dioxomolybdenum(VI) compounds in dichloromethane and H_2O_2 (30 % (by weight)) + H_2O solution were measured respectively. To the best of our knowledge, no such data have been reported in the literature.

Experimental Section

Materials. All the chemicals in the synthesis and measurement were analytical grade reagents. $OPPh_3$ and $OPMePh_2$ were purchased from Alfa Aesar and Aldrich, respectively. The other chemicals were purchased from the Beijing Chemical Reagents Company. They were used without further purification.

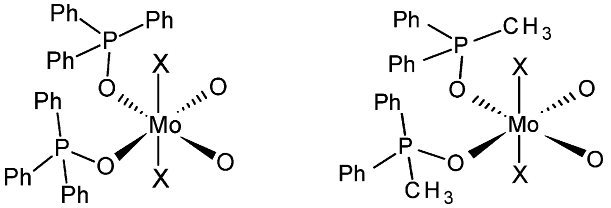

Figure 1. The structure of $MoO_2X_2L_2$ (X = Cl, Br; L = $OPPh_3$, $OPMePh_2$).

Apparatus and Procedure. The melting points were measured by a SGW-X-4 micromelting point apparatus. The elemental analysis was performed on an Elementar Vario Micro Cube element analyzer. IR spectra (Fourier transform infrared (FT-IR)) were recorded on a VECTOR22 using KBr pellets. ^1H NMR spectra were recorded on a Varian Unity Inova-400 spectrometer. ^{31}P NMR spectra were recorded on a JEOL JNM ECA-600 spectrometer operating at 242.95 MHz with $CDCl_3$ inside using the standard pulse sequence at room temperature.

A jacketed equilibrium cell was used for the solubility measurements with a working volume of 120 mL and a magnetic stirrer, as described by Wang et al.[9,10] A circulating water bath was used with a thermostat (type 50 L, made by the Shanghai Laboratory Instrument Works Co., Ltd.), which is capable of maintaining the temperature within ± 0.05 K. An analytic balance (type TG328B, Shanghai Balance Instrument Works Co.) with an uncertainty of ± 0.1 mg was used during the mass measurements.

Synthesis of Dioxomolybdenum Complexes. $MoO_2X_2L_2$ (X, L = Cl, $OPPh_3$ (**1**); Br, $OPPh_3$ (**2**); Cl, $OPMePh_2$ (**3**); Br, $OPMePh_2$ (**4**)) were prepared according to the literature.[5] Molybdic acid was dissolved in the appropriate concentrated hydrohalic acid, and a solution of the phosphine oxide dissolved in the minimum amount of ethanol was added. The mixture was stirred at room temperature (rt) for 30 min and the resulting precipitate was filtered, dried under vacuum at rt and washed with hexanes. The product was then recrystallized from dichloromethane. Yield: 61 % **1**, 62 % **2**, 66 % **3**, and 65 % **4**. mp: (261 to 263) °C for **1**, (280 to 282) °C for **2**, (181 to 182) °C

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Table 1. Mole Fraction Solubilities (x) of Dioxomolybdenum(VI) Complexes in Dichloromethane and H_2O_2 (30 % (By Weight)) + H_2O Solution

	dichloromethane		H_2O_2 (30 % (by weight)) + H_2O solution	
complexes	T/K	x	T/K	x
1	283.16	0.00689	298.16	0.00007
	286.05	0.00754	303.05	0.00010
	289.23	0.00861	308.63	0.00015
	292.45	0.00999	313.45	0.00019
	295.51	0.01129	318.51	0.00026
	298.55	0.01246	323.55	0.00034
	301.71	0.01446	328.70	0.00043
	304.64	0.01548	333.64	0.00056
	307.42	0.01722	338.71	0.00070
	310.39	0.01967	343.56	0.00089
			348.79	0.00110
			353.93	0.00144
			358.82	0.00174
2	283.35	0.00624	298.25	0.00006
	286.56	0.00713	303.32	0.00008
	289.43	0.00782	308.24	0.00010
	292.61	0.00885	313.49	0.00014
	295.48	0.00972	318.50	0.00017
	298.32	0.01105	323.37	0.00023
	301.39	0.01256	328.51	0.00029
	304.31	0.01432	333.63	0.00036
	307.47	0.01561	338.57	0.00047
	310.41	0.01782	343.80	0.00059
			348.68	0.00074
			353.73	0.00091
			358.41	0.00105
3	283.21	0.00968	298.20	0.00014
	286.05	0.01133	303.13	0.00019
	289.17	0.01267	308.52	0.00028
	292.12	0.01344	313.61	0.00038
	295.35	0.01534	318.27	0.00050
	298.29	0.01712	323.39	0.00066
	301.43	0.01893	328.56	0.00091
	304.60	0.02102	333.49	0.00116
	307.46	0.02382	338.52	0.00146
	310.28	0.02616	343.70	0.00191
			348.86	0.00244
			353.77	0.00331
			358.74	0.00412
4	283.17	0.00867	298.02	0.00012
	286.24	0.00928	303.19	0.00015
	289.36	0.01041	308.22	0.00022
	292.54	0.01257	313.36	0.00031
	295.49	0.01347	318.21	0.00042
	298.21	0.01543	323.27	0.00054
	301.16	0.01638	328.18	0.00071
	304.38	0.01823	333.45	0.00096
	307.44	0.02051	338.46	0.00125
	310.38	0.02334	343.22	0.00163
			348.50	0.00204
			353.67	0.00268
			358.79	0.00330

for **3**, and (205 to 207) °C for **4**. Elemental analysis (%, calculated): C, 57.18 (57.24), H, 4.05 (4.00) for **1**; C, 51.32 (51.18), H, 3.61 (3.55) for **2**; C, 49.29 (49.45), H, 4.06 (4.12) for **3**; C, 42.98 (43.09), H, 3.47 (3.59) for **4**. IR 948 (s) cm^{-1} and 905 (s) cm^{-1} for **1**, 944 (s) cm^{-1} and 900 (s) cm^{-1} for **2**, 947 cm^{-1} and 903 (s) cm^{-1} for **3**, 941 (s) cm^{-1} and 895 (s) cm^{-1} for **4**. ^1H NMR ($CDCl_3$) ppm: $\delta = 7.26$ to 7.77 (m, 30 H, Ph) for **1**; $\delta = 7.27$ to 7.78 (m, 30 H, Ph) for **2**; $\delta = 2.21$ (δ, $J = 14.1$ Hz, 6 H, CH_3) and 7.26 to 7.78 (m, 20H, Ph) for **3**; $\delta = 2.27$ (δ, $J = 14.1$ Hz, 6 H, CH_3), 7.27 to 7.83 (m, 20H, Ph) for **4**; $\delta = 7.44$ to 7.69 for $OPPh_3$, $\delta = 2.02$ (δ, $J = 14.1$ Hz, 3 H, CH_3) and 7.45 to 7.74 (m, 10H, Ph) for the $OPMePh_2$ ligand. ^{31}P NMR ($CDCl_3$) ppm: $\delta = 40.2$ for **1**, $\delta = 41.8$ for **2**, $\delta = 44.7$ for **3**, $\delta = 45.5$ for **4**, $\delta = 29.8$ for $OPPh_3$, and $\delta = 30.6$ for the $OPMePh_2$ ligand.

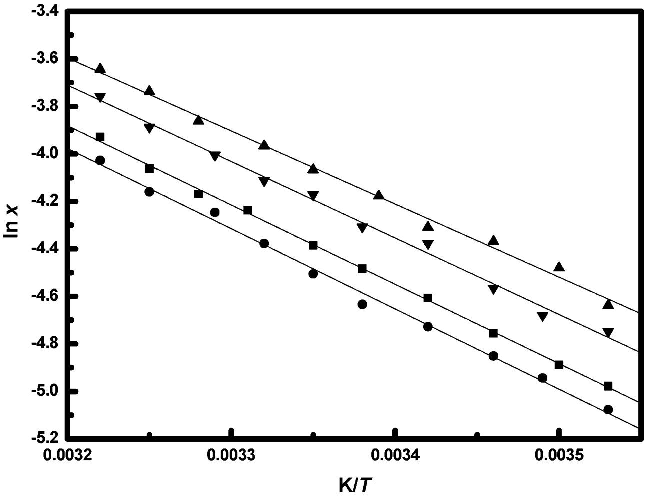

Figure 2. Mole fraction solubilities of dioxomolybdenum(VI) complexes in dichloromethane: ■, **1**; ●, **2**; ▲, **3**; ▼, **4**; –, solubility curve calculated from eq 3.

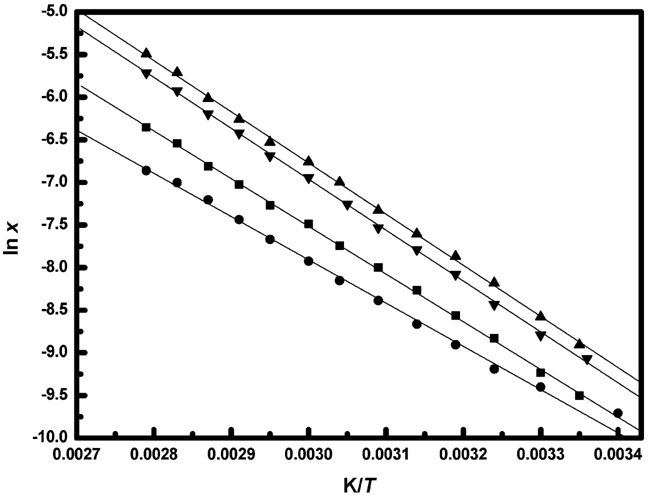

Figure 3. Mole fraction solubilities of dioxomolybdenum(VI) complexes in H_2O_2 (30 % (by weight)) + H_2O solution: ▼, **1**; ●, **2**; ▲, **3**; ■, **4**; –, solubility curve calculated from eq 3.

Table 2. Parameters of Equation *3* and Root-Mean-Square Deviations of the Measured Solubility Calculated from Equation *4* for Dichloromethane and H_2O_2 (30 % (by weight)) + H_2O Solution

solvent	complexes	A	B	RSD
dichloromethane	**1**	6.8007	−3338.2	0.015
	2	6.8325	−3378.0	0.018
	3	6.2496	−3076.7	0.015
	4	6.5920	−3219.5	0.026
H_2O_2 (30 % (by weight)) + H_2O solution	**1**	9.2746	−5596.8	0.024
	2	7.3211	−5076.7	0.026
	3	11.2344	−6002.1	0.027
	4	10.9623	−5975.0	0.021

Solubility Measurement. The solubilities were measured by a gravimetric method.[9,10] For each measurement, an excess mass of dioxomolybdenum(VI) complexes was added to a known mass of dichloromethane and H_2O_2 (30 % (by weight)) + H_2O solution. Then the equilibrium cell was heated to a constant temperature with continuous stirring. After at least 2 h (the temperature of the water bath approached a constant value, then the actual value of temperature was recorded), the stirring was stopped and the solution was kept still until it was clear. A preheated on−off injector with a cotton filter withdrew 2 mL of the clear upper portion of the solution to another previously weighed measuring vial (m_0). The vial was quickly and tightly closed and weighed (m_1) to determine the mass of the sample ($m_1 - m_0$). Then the vial was uncovered with a piece of filter paper to prevent dust contamination. After the solvent in the vial had completely evaporated, the vial was dried and reweighed (m_2) to determine the mass of the constant residue solid ($m_2 - m_0$). Thus, the solid concentration of the sample solution in mole fraction, x, could be determined from eq 1[11]

$$x = \frac{(m_2 - m_0)/M_1}{(m_2 - m_0)/M1 + (m_1 - m_2)/M_2} \qquad (1)$$

Equation 1 is for pure solvent, where M_1 is the molar mass of dioxomolybdenum(VI) complex and M_2 is the molar mass of dichloromethane.

$$x = \frac{(m_2 - m_0)/M_1}{(m_2 - m_0)/M_1 + (m_1 - m_2)w_2/M_2 + (m_1 - m_2)(1 - w_2)/M_3} \qquad (2)$$

Equation 2 is for a mixed solvent, where M_1, M_2, and M_3 are the molar mass of the dioxomolybdenum(VI) complex, H_2O_2 and H_2O, respectively, and w_2 is the mass of fraction of H_2O_2 in the water.

Different dissolution times were tested to determine a suitable equilibrium time. It was found that 2 h was enough for dioxomolybdenum(VI) complexes in dichloromethane or H_2O_2 (30 % (by weight)) + H_2O solution to reach equilibrium. The estimated relative uncertainty of the solubility values based on error analysis and repeated observations was within 0.02.

Results and Discussion

The complexes **1** to **4** as catalysts were chosen for epoxidation of olefins because they are easy to prepare and unreactive with air or water. Furthermore, they provide a good basis for understanding how changes in the electronic and steric environment of the complexes resulting from altering the halides and phosphine oxide ligands, affect the catalytic activity.

The IR spectra of **1** to **4** show two strong bands at about (900 and 950) cm^{-1}, arising from symmetric and asymmetric MoO_2 stretching vibrations, respectively.[12]

^1H NMR spectra of the $OPPh_3$ and $OPMePh_2$ ligand displayed a multiplet in the range (7.4 to 7.7) ppm assigned to the hydrogen atoms of the phenyl rings and 2.02 ppm assigned to the methyl hydrogens of $OPMePh_2$. The ^1H NMR spectra of **1** to **4** were observed to shift upfield only slightly to (7.2 to 7.7) ppm. This increased shielding is probably due to the removal of the H-bonded interactions as the free ligand may also exist in solution as a dimer. In contrast, the resonance for the $OPMePh_2$ ligand in **3** and **4** shifted downfield only slightly to (2.21 and 2.27) ppm, respectively.

^{31}P NMR spectroscopy is very useful in assessing the composition and purity of compounds bearing phosphorus atoms.[13] The ^{31}P NMR shift of uncoordinated phosphine oxide $OPPh_3$ and $OPMePh_2$ are (29.8 and 30.6) ppm, respectively. Because of coordination via the O atom (bonded to the P atom), **1** to **4** each reveals a single resonance ca. 10 ppm to high frequency of the corresponding uncoordinated phosphine oxide ligand. The $MoO_2Cl_2L_2$ species **1** and **3** shifts downfield to 40.5 ppm for L = $OPPh_3$ and 44.7 ppm for L = $OPMePh_2$, and the corresponding resonance for the bromo analogues **2** and **4** are observed at 41.8 ppm for L = $OPPh_3$ and 45.5 ppm for L = $OPMePh_2$, respectively. The single resonance suggests that the P atoms are magnetically equivalent in these compounds at least in solution. Furthermore, the ^{31}P NMR shift of the Mo-chloro complexes **1** and **3** are consistently at a higher frequency than the bromo analogues **2** and **4** by ca. 1 ppm. This very small difference indicates that the electronic environment at Mo(VI) is little influenced by X and L (or L−L), but is probably dominated by the Mo-dioxo unit as expected.

The mole fraction solubility data of dioxomolybdenum(VI) complexes, x, in dichloromethane and H_2O_2 (30 % (by weight)) + H_2O solution are summarized in Table 1 and plotted as $\ln x$ versus temperature in Figures 2 and 3. From these figures, it can be seen that a trend of increasing solubility with temperature is observed, and the solubilities of these dioxomolybdenum(VI) complexes decrease in the order **3** > **4** > **1** > **2**, which is in accordance with the size of the molar mass of these complexes, indicating that dioxomolybdenum(VI) complexes containing a smaller ligand and volume of halogen atom give higher solubilities. The solubility of complex **3** in dichloromethane at 310.28 K is 19.9 (g/100 g of solvent). In a H_2O_2 (30 % (by weight)) + H_2O solution, the solubility of complex **3** at 358.74 K is 3.1 (g/100 g of solvent).

The solubilities were correlated as a function of temperature by

$$\ln x = A + B/(T/\mathrm{K}) \qquad (3)$$

Parameters A and B for each solvent are listed in Table 2. The relative standard deviations (RSD), defined by eq 4, are also presented in Table 2.

$$\mathrm{RSD} = \left[\frac{1}{N}\sum_{1}^{n}\left(\frac{x_i - x_i^{\mathrm{calcd}}}{x_i}\right)^2\right]^{1/2} \qquad (4)$$

where calcd stands for the calculated values and N is the number of experimental points. The smoothed data calculated from eq 3 are compared with the data listed in Table 1, and the results are shown in Figures 2 and 3.

The results show that eq 3 can be used to correlate the solubility data. The relative standard deviations of measured solubilities from the smoothed data in dichloromethane are 0.015 for **1**, 0.018 for **2**, 0.015 for **3**, and 0.026 for **4**, and those in H_2O_2 (30 % (by weight)) + H_2O solution are 0.024 for **1**, 0.026 for **2**, 0.027 for **3**, and 0.021 for **4**.

The solubilities of these dioxomolybdenum(VI) complexes in H_2O_2 decrease in the order **3** > **4** > **1** > **2**, which may result in the same order to their catalytic activity in olefin epoxidation with H_2O_2 as oxidant.

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