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Photochemical reactions of group 6 metal carbonyls with *N*-salicylidene-2-hydroxyaniline and bis-(salicylaldehyde)phenylenediimine

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Abstract

Sunlight irradiation of the reactions of $[M(CO)_6]$, M=Cr, Mo and W with either *N*-salicylidene-2-hydroxyaniline (shaH₂) or bis-(salicylaldehyde) phenylenediimine (salphenH₂) in THF were investigated. Three complexes with molecular formulas $[Cr(shaH_2)_3]$, **1**, $[MoO_2(shaH_2)_2]$, **2**, and $[W_2O_5(shaH)_2]$, **3** were isolated from the reactions with shaH₂. The corresponding reactions with salphenH₂ produced the oxo complexes $[CrO(salphenH_2)]$, **4**, $[Mo_2O_6(salphenH_2)_2]$, **5**, and $[W_2O_6(salphenH_2)]$, **6**. All complexes were characterised by elemental analysis, infrared, mass and ¹H NMR spectroscopy. The UV–vis spectra of the complexes in different solvents showed visible bands due to either ligand-to-metal or metal-to-ligand charge transfer. Thermal properties of the complexes were investigated by TG thermogravimetry technique.

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1. Introduction

A large number of Schiff base compounds are often used as ligands in coordination chemistry for their metal binding ability. Schiff base-metal complexes are characterised by interesting and important properties, such as their ability to reversibly binding oxygen in epoxidation reactions [1], biological activity [2–5], complexing ability towards some toxic metals [6], catalytic activity in hydrogenation of olefines [7] and photochromic properties [8,9]. Polydentate Schiff bases containing nitrogen and oxygen donor atoms such as bis-(salicylaldehyde)ethylenediimine (salenH₂), bis-(salicylaldehyde)phenylenediimine (salphenH₂), salicylideneimine-2-anisole (salanH), and *N*-salicylidene-2hydroxyaniline (shaH₂) are useful for the synthesis of transition metal complexes which play important role in biological systems [10,11]. Such classes of ligands were also found to provide catalytic characteristics especially for epoxidation reactions [12–17].

Reactions of group 6 and 8 metal carbonyls with some selected Schiff bases having oxygen and nitrogen donors were investigated [18–20]. Reactions of the two Schiff bases, $shaH_2$ and salphenH₂, with [M(CO)₆], M=Cr, Mo and W gave complexes with different structural features; [CrO₂(CO)₂ ($shaH_2$)], [W(CO)₂($shaH_2$)], [Cr(CO)₂(slaphen)], [MoO (CO)(salphen)], [MoO(sha)], [MoO(sha)], [MoO₂($shah_2$)], [MoO₂($slaphenH_2$)] and [W₂O₆($salphenH_2$)] [21,22]. The versitile chemistry of these reactions has prompted us to investigate the reactions of Group 6 metal carbonyls with $shaH_2$ and salphenH₂, Scheme 1, under sunlight photolysis.

2. Experimental

2.1. Reagents

 $[M(CO)_6]$, M=Cr, Mo and W were supplied by Aldrich. The shaH₂ and salphenH₂ ligands were prepared

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as described in literatures [21,23]. All solvents were purified by distillation before use.

2.2. Instruments

Infrared measurements (KBr pellets) were carried out on a Unicam–Mattson 1000 FT-IR spectrometer. UV–vis spectra were measured on a Unicam UV2-300 spectrophotometer. NMR measurements were performed on a Spectrospin– Bruker AC 200 MHz spectrometer. Samples were dissolved in deuterated DMSO using TMS as internal reference. Elemental analyses were performed on a Perkin–Elmer 2400 CHN elemental analyzer. Mass spectrometry measurements of the solid complexes (70 eV, EI) were carried out on a Finnigan MAT SSQ 7000 spectrometer. Thermogravimetric analysis was performed under nitrogen atmosphere with a heating rate of 10 °C/min using a Schimadzu DT-50 thermal analyzer. Table 1 gives the elemental analysis and mass spectrometry data for the complexes.

2.3. Syntheses of complexes

A general procedure was employed for the synthesis of the reported complexes. A mixture of equimolar amounts of $[M(CO)_6]$, M=Cr, Mo and W, and either shaH₂ or salphenH₂ in a sealed tube containing 25 cm³ of THF. Photolysis of the mixture with sunlight for a certain period of time (25 °C) was employed (Table 1). (The photoexcitation procedure is expected to be the UV range of light). The solvent was removed on a vacuum line. The residue was washed several times by boiling petroleum ether and then recrystallized from THF. The complex was left to dry in vacuo for several hours. Table 1 gives the reaction period, color of complex and % yield.

3. Results and discussion

3.1. Infrared and NMR studies

3.1.1. The shaH₂ complexes

Interaction of $[M(CO)_6]$, M=Cr, Mo and W, with Nsalicylidene-2-hydroxyaniline (shaH₂) under sunlight irradiation resulted in the formation of different complexes depending on the metal type. While the reaction with $[Cr(CO)_6]$ gave the tris derivative $[Cr(shaH_2)_3]$, 1, with the chromium atom in the zero formal oxidation state, the molybdenum and tungsten hexacarbonyls gave the oxo derivatives [MoO₂(shaH₂)₂], **2**, and [W₂O₅(shaH)₂], **3**, with +4 and +6 formal oxidation states, respectively. It is expected that the formation of complexes were proceeded via the M(CO)₅ intermediate through M–CO bond dissociation. This is a general route for the UV photolysis of the hexacarbonyls of Group 6 [24]. Such intermediate reacts with either the ligand alone to give the chromium derivative or with the ligand and oxygen to give the molybdenum and tungsten products. The source of oxygen in the oxo complexes could be originated from the dissolved oxygen in the used solvent. It is well established that both molybdenum and tungsten have higher affinity to react with oxygen [24,25]. Numerous oxo molybdenum and tungsten complexes were previously reported. For example, interaction of bis-(salicylaldehyde)etylenediimine (salenH₂) and 2-hydroxyacetophenoneethylenediimine (hapenH₂) with $Mo(CO)_6$ in THF under atmospheric pressure gave Mo(O)(salen) and Mo(O)(happen) with the metal atom in +4 oxidation state [18,19]. Also, reactions of the Schiff base salicylideneimine-2-anisole (salanH) with $M(CO)_6$, M = MOor W, gave the dinuclear oxo complex $M_2O_4(salan)_2$ [26]. The infrared spectrum of the chromium complex, 1, displayed the characteristic bands of shaH₂ with the appropriate shifts due to complex formation (Table 2). The complex showed vibrational bands at 3354, 1379 and 1340 cm⁻¹ due to ν (OH) and δ (OH) frequencies, respectively (Table 2). In addition, the infrared spectrum of 1 showed an appreciable shifts in the ν (C=N) and ν (C-O)

Table 1

Elemental analysis and mass spectrometry data for the chromium, molybdenum and tungsten complexes

Complex	Color	Reaction	% Yield	Elementa	Elemental analysis						trometry
		time (h)		%C		%H	%H		%N		$m/z (p^+)$
				Calc.	Found	Calc.	Found	Calc.	Found	-	
1	Brown	3	73	67.7	67.4	4.8	5.0	6.1	5.9	691.7	692
2	Dark-brown	4	68	56.3	56.1	4.0	4.2	5.7	5.5	554.4	555
3	Light-brown	10	75	35.8	35.6	2.3	2.4	3.2	3.0	872.2	873
4	Brown	6	84	62.5	62.3	4.2	4.5	7.3	7.1	384.4	385
5	Dark-brown	5	61	52.2	52.4	3.5	3.1	6.1	6.2	920.6	921
6	Light-brown	12	53	30.8	30.4	2.1	1.9	3.6	3.4	780.1	781

Table 2 Infrared data for the shaH₂, salphenH₂ and their chromium, molybdenum and tungsten complexes

Compound	Infrared data	Infrared data $(cm^{-1})^a$										
	$\nu(C=N)$	ν(C–O)	$\delta(OH)$	<i>ν</i> (OH)	ν(M=O)	ν(M–O–M)	ν(M–O)	ν(M–N)				
shaH ₂	1631 (s)	1274 (m)	1368 (m)	3422(m)	_	_	_	_				
		1243 (m)										
1	1607 (s)	1278 (m)	1379 (m)	3354 (m,b)	_	_	534(m)	420(m)				
		1146 (m)	1340 (m,sh)									
2	1612 (s)	1281 (m)	1389 (m)	3384 (m,b)	933(s)	-	551(m)	477(w)				
		1247 (m)	1371 (m,sh)		912(s)							
3	1613(s)	1286 (m)	1385(m)	3381(m,b)	946(s)	642(m)	554(w)	444(m)				
		1241 (m)			899(m)							
salphenH ₂	1612(s)	1274(s)	1455 (m)	3424 (m)	_	_	_	_				
4	1605(s)	1278(s)	1441 (m)	3383 (m,b)	853(s)	-	539(m)	453(m)				
			1461(m)									
5	1605(s)	1282 (m)	1462 (m)	3283 (m)	937(m)	799(m)	548(m)	470(w)				
					914(s)	652(m)						
6	1606(s)	1256(m)	1454(m)	3198(m)	979(s)	633(m)	588(m)	444(w)				
					895(s)	507(w)						
					818(m)	. /						

^a s, strong; m, medium; b, broad; sh, shoulder.

bands. The infrared spectrum of the complex also exhibited two non-ligand bands at 534 and 420 cm⁻¹ due to Cr–O and Cr–N bonds, respectively [19,27]. Therefore, it can be concluded that shaH₂ ligand probably coordinated to chromium atom through phenolic oxygen and azomethine nitrogen and acting as a bidentate ligand. From the elemental analysis and spectroscopic data, it can be concluded that the chromium complex has the tris configuration as shown in Scheme 2. This structural arrangement would give a chromium species with zero (d⁶) oxidation state. Magnetic studies of the complex showed paramagnetic characteristics. The magnetic measurement at 298 K gave a value of 2.98 BM for the effective magnetic moment. This value is close to the spin-only moment of two unpaired electrons (2.84 BM). Since the UV–vis of the complex [Cr(shaH₂)₃] did not display the characteristic band of the high-spin configuration at 628 nm (vide infra) and the value of the μ_{eff} is in the range 2.7–3.4 BM, it is suggested that the complex has the electronic configuration $d_{xz}^2 d_{yz}^1 d_{xy}^1 d_z^1 d_{x2-y2}^0$ [22]. Thus, this μ_{eff} value could be due to second order paramagnetism effects arising from a low lying excited state in an otherwise diamagnetic compound; the diamagnetism might arise from further splitting of the t_{2g} orbitals in the low symmetry complex [19].



Scheme 2. The shaH₂ complexes.

The sun irradiation of a mixture of [Mo(CO)₆] and shaH₂ in THF produced the mononuclear dioxo complex [MoO₂ $(shaH_2)_2$, 2, with the metal atom in +4 formal oxidation state. The corresponding thermal reaction gave a dinuclear derivative $[Mo_2O_4(sha)_2]$ with the molybdenum in the +6 formal oxidation state [21]. The infrared spectrum of 2 displayed the ligand bands with the corresponding shifts due to complex formation, Table 2. In addition, two stretching bands were observed at 933 and 912 cm^{-1} due to symmetric and asymmetric frequencies of two terminal cis Mo=O bonds [28]. The infrared spectrum of the molybdenum complex also displayed non-ligand bands at 551 and 477 cm⁻¹ due to Mo-O and Mo-N bonds, respectively. Furthermore, the infrared spectrum showed a broad band at 3384 cm^{-1} due to stretching OH frequencies, and two bands at 1389 and 1371 cm^{-1} due to bending OH frequencies. The ¹H NMR spectrum of **2** displayed two signals at 13.69 and 10.67 ppm indicating the presence of two OH groups. The latter signal showed lower field shift and indicated that the shaH₂ ligand coordinated to the molybdenum atom through the OH group, which is cis to the azomethine group. The other OH signal at 13.69 ppm was broad and showed a higher field shift relative to that of ligand, which may indicate the presence of hydrogen bonding as in Scheme 2.

Interaction of $[W(CO)_6]$ with $shaH_2$ under sunlight irradiation resulted in the formation of a light-brown complex with a molecular formula of $[W_2O_5(shaH)_2]$, **3**. The infrared spectrum of the tungsten complex showed the ligand bands with appropriate shifts as a result of complex formation (Table 2). The C=N stretching vibration of the tungsten complex displayed a shift of 18 cm^{-1} to lower energy relative to that of ligand (Table 2) indicating the coordination of the azomethine nitrogen atom to the metal [12]. The infrared spectrum of 3 also displayed two vibrational bands at 946 and 899 cm⁻¹ due to symmetric and asymmetric frequencies of two terminal cis W=O bonds. In addition, stretching infrared bands were observed at 642, 554 and 444 cm^{-1} corresponding to W–O–W, W–O and W-N bonds, respectively. Interestingly, the infrared spectrum of the tungsten complex exhibited only one bending OH band due to one OH group, which is different from the chromium and molybdenum derivatives (Table 2). This could be probably due to coordination of one OH group to the metal with proton displacement, i.e., the ligand reacted oxidatively. The presence of OH bands in the infrared spectrum of the complex due to the other OH group with low frequency shift indicated the presence of intramolecular hydrogen bonding (Scheme 2).

3.1.2. The salphen H_2 complexes

Interaction of $[M(CO)_6]$, M=Cr, Mo and W, with bis-(salicylaldehyde)-phenylenediimine (salphenH₂) in THF under sunlight irradiation gave the oxo complexes $[CrO(salphenH_2)]$, **4**, $[Mo_2O_6(salphenH_2)_2]$, **5**, and $[W_2O_6(salphenH_2)_2]$, **6**. Scheme 3 gives the proposed structures for the complexes. The infrared spectrum of salphenH₂ displayed the characteristic bands due to OH, C–O, and C=N function groups (Table 2). The infrared spectrum of the chromium complex, **4**, exhibited the ligand bands with the corresponding shifts, Table 2. It also displayed two bands at 1441 and 1461 cm⁻¹ due to δ (OH) vibrations and a broad



Scheme 3. The salphenH₂ complexes.

band at 3383 cm⁻¹ due to a ν (OH) stretching frequency. The shift in these OH bands relative to those of ligand indicated that the two OH groups may be coordinated to chromium atom without proton displacement and forming hydrogen bonding with the oxygen atom. In addition, the infrared spectrum of **4** showed additional bands at 539 and 453 cm⁻¹ due to ν (Cr–O) and ν (Cr–N), respectively. The appearance of a strong infrared band at 853 cm^{-1} could be attributed to ν (Cr=O) stretching vibration. Investigation of the chromium complex by ¹H NMR spectroscopy gave no signals due to its paramagnetic properties. It is expected that chromium would have a $Cr(II) d^4$ electronic configuration (Scheme 3). Magnetic measurement of 4 at 298 K gave a value of an effective magnetic moment of 3.9 BM. This value is less than the spin only value for four unpaired electrons (4.8 BM). Many paramagnetic chromium complexes exhibited effective magnetic moment values less than the spin-only ones [22]. Magnetic studies of the two complexes [Mo(O)(salen)] [18] and [Mo(O)(hapen)] [19] with metal atom in +4 formal oxidation state gave μ_{eff} values less than the spin-only value of two unpaired electrons.

Reaction of $[Mo(CO)_6]$ with salphenH₂ under sunlight irradiation resulted in the formation of the dark-brown oxo complex [Mo₂O₆(salphenH)₂], **5**. The infrared spectrum of **5** displayed the ligand bands with the proper shifts indicating complex formation (Table 2). In addition, the infrared spectrum exhibited two bands at 937 and 914 cm^{-1} due to symmetric and asymmetric stretching vibrations of O=Mo=O indicating that the two oxygen atoms were coordinated to the metal in cis positions. Further more, another two bands at 799 and 652 cm^{-1} were observed due to ν (Mo–O–Mo) frequencies [29,30]. The infrared spectrum of $[Mo_2O_6(salphenH)_2]$ displayed a band at 3283 cm⁻¹ due to $\nu(OH)$ and a band at 1462 cm⁻¹ due to $\delta(OH)$. The presence of the OH groups was also confirmed by ¹H NMR spectroscopy. The OH signals displayed shifts to the higher field. The shift in the ¹H NMR signals and the IR bands indicated that the OH groups formed intra- and intermolecular hydrogen bonding (Scheme 3). Magnetic measurements showed diamagnetic properties for 5. According to the proposed structure, molybdenum may have +6 formal oxidation state with d⁰ electronic configuration.

On comparison between the complex formed from sunlight irradiation reaction, $[Mo_2O_6(salphenH)_2]$, and the corresponding derivative formed via thermal reaction, $[MoO_2(salphenH)_2]$, different structural arrangement were observed [22]. The former complex is a dinuclear with the two salphenH moieties bound to the metal through their nitrogen atoms while the later complex is a mononuclear with the two salphenH moieties bound to the metal through nitrogen and oxygen atoms [22].

Reaction of $[W(CO)_6]$ with salphenH₂ under sunlight irradiation gave the light brown oxo complex $[W_2O_6$ (salphenH₂)], **6**. The infrared and ¹H NMR spectra of the complex showed that the complex is identical to that isolated from the thermal reaction [22] (Table 3). Table 3

¹H NMR data of shaH₂ and salphenH₂ and their chromium, molybdenum and tungsten complexes

Compound	¹ H NMR data (ppm) ^a
shaH ₂	13.75 (s, OH), 9.70 (s, OH), 9.03 (s, N=CH),
	7.55 (m, Ph), 7.06 (m, Ph)
2	13.69 (s, OH), 10.67 (s, OH), 9.66 (s, N=CH),
	7.36–6.84 (m, Ph)
3	9.27 (s, N=CH), 7.87-6.88 (m, Ph)
salphenH ₂	12.86 (s, OH), 8.93 (s, CH), 7.65 (m, Ph),
	7.43 (m, Ph), 6.94 (m, Ph)
5	10.70 (s, OH), 10.25 (s, OH), 9.11 (s, N=CH),
	7.67–7.72 (m, Ph)
6	9.95 (s, OH), 9.08 (s, N=CH), 7.65-6.70 (m, Ph)

^a s, singlet; m, multiplet.

3.2. UV–vis studies

The electronic absorption studies of shaH₂, salphenH₂ and their complexes were studied in DMSO, CH₂Cl₂, acetone, benzene and methanol (Table 4). The UV-vis spectra of the shaH₂ ligand displayed two absorption bands in all solvents. The first absorption band ranged from 268 to 278 nm was corresponded to $\pi - \pi^*$ electronic transitions. The second band at 349–357 nm was due to $n-\pi^*$ transition. In the complexes, a bathochromic shift in the π - π * electronic transition was observed, Table 4. On the other hand, the $n-\pi^*$ electronic transitions exhibited hypsochromic shifts. The complexes showed additional absorption bands in the range 404-480 nm which could be due to charge transfer transitions, Table 4. In the chromium complex, metal-to-ligand charge transfer (shaH₂ $\pi^* \leftarrow Cr$ $d\pi$) could be assigned while in molybdenum and tungsten complexes, ligand-to-metal charge transfer (M d π \leftarrow shaH₂ π^*) might be present [31].

Similar to those of shH₂, the UV–vis absorption spectra of salphenH₂ gave two absorption bands in all solvents. The first absorption band referred to π – π * electronic transitions and ranged from 260 to 274 nm. On the other hand, the second absorption band ranged from 328 to 348 nm was corresponded to n– π * electronic transition. On going from salphenH₂ ligand to its complexes a bathochromic shifts were exerted in the π – π * electronic transitions, Table 4. On the other hand, the n– π * electronic transitions exhibited hypsochromic shifts (Table 4). All complexes displayed additional absorption bands in the range 359–540 nm corresponding to (M d π ← salphenH₂ π *) charge transfer [28].

3.3. Thermogravimetric analysis

In order to give more insight into the structure of the complexes, the thermal studies of the complexes were carried out using thermogravimetry (TG) technique. The TG plot of $Cr(shaH_2)_3$ displayed three resolved and well-defined decomposition steps. The first decomposition step occurred in the temperature ranges 298–502 K, with a net

omoduno	DMSO			CH°CI2			Acetone			Benzene			CH ₂ OH		
				7-77-17									C113011		
	π−π*	$n_{-\pi^*}$	CT	$\pi\pi^*$	$n-\pi^*$	CT	$\pi_{-}\pi^{*}$	$n-\pi^*$	CT	モーカ*	$n-\pi^*$	CT	$\pi\pi^*$	$n{-}\pi^*$	СT
haH ₂	272	356	I	270	357	I	278	357	I	268	I	I	269	349	I
	275	356	450(b)	273	329(b)	443(b)	274	345	435	268	352(b)	448(b)	272	355(sh)	439(b)
									480(sh)						
	274	353	434(b)	267	325(b)	432(b)	270	347	424(sh)	276	351	432(b)	273	355	434(b)
								321							
	276	350	404(b)	273	323	422	269	362	404	280	340	434(b)	280	355	405
								322							
alphenH ₂	273	328	I	271	I	I	260	346	I	274	348	I	267	330(b)	I
	260	397(sh)	474(sh)	273	319	468(sh)	262	325	469(sh)	276	335	467(sh)	230	315	458
	275	367	489(b)	274	311(sh)	540(b)	264	326	478(sh)	272	321	480(sh)	270	320	470
	272	332	359(sh)	274	316(sh)	454(b)	268	320	473	277	329	472	269	325	460

weight loss of 13.05%, probably due to elimination of three C_2H_6 moieties, Table 5. The second decomposition step occurred in the temperature range 502–626 K with a net weight loss of 15.23% due to the loss of a NO₂ and C_4H_{11} moieties. The third decomposition step (626–1141 K, 62.31%) was due to the elimination of $C_{29}H_4N_2O_3$ species to leave the metallic residue CrO (Table 5).

The TG plot of the MoO₂(shaH₂)₂ complex displayed four decomposition steps in the temperature range 365– 1000 K (Table 5). The first decomposition step occurred in the temperature range 365–413 K with a net weight loss of 8.50% corresponding to elimination of a C₃H₁₁. The second decomposition peak occurred in the temperature range 413– 548 K with a weight loss of 17.34% and corresponded to the material decomposition of C₆H₈O. The third decomposition step in the temperature range 548–714 K is corresponded to the elimination of a NO species. The last decomposition step at the temperature range 714–1000 K is due to the elimination of C₁₇H₃ and NO₂ moieties to give finally the metallic residue MoO₂.

The W₂O₅(shaH)₂ complex was found to thermally decompose in three well-defined steps in the temperature range 323–965 K (Table 5). The first decomposition step at 323–590 K with a net weight loss of 66.98% corresponded to elimination of C₅H₇ species molecules. The second decomposition step (590–735 K, 16.60%) was due to elimination of C₆H₁₀O species and NO₂ molecule. The third decomposition step occurred in the temperature range 735–965 K (weight loss 22.61%) probably due to the elimination of a C₁₅H₃N moiety to leave WO₃ as a residue.

The TG plot of $CrO(salphenH_2)$ showed that it decomposed in two steps. The first decomposition step (323–603 K, 15.62%) was due to the elimination of two NO molecules. The second step at 603–703 K with a net weight loss of 70.87% was due to material decomposition to leave the chromium metal as a residue (13.53%).

The complex Mo₂O₆(salphenH₂) was decomposed in three steps. In the range 348–713 K, the complex was firstly decomposed with a net weight loss of 30.98% due to the elimination of $C_{15}H_{13}$ moiety in addition to two NO₂ molecules. The second decomposition step in the range 713–933 K was found to be due to the elimination of $C_{13}H_{12}$ species and two NO₂ molecules. The third decomposition step at 933–1073 K was corresponded to the elimination of $C_{12}H_7$ species leaving MoO as metallic residue.

The TG plot of $W_2O_6(\text{salphenH}_2)$ complex gave five decomposition steps in the range 328–1073 K. The first three steps at 328–693 K were overlapped and unresolved. They could be corresponded to the elimination of C_5H_6 moiety and NO₂ molecule (14.37%). The fourth decomposition step at 693–833 K corresponded to the elimination of C_4H_7 species (7.06%), while the fifth step (833–1073 K) was corresponded to the elimination of $C_{11}H_3$ moiety and NO₂ molecule leaving WO₂ as metallic residue.

Γable ₄

Table 5 Thermal analysis data for the chromium and molybdenum complexes of shaH₂ and salphenH₂

Complex	Decomposition step, K	% Weight loss	Mol. wt.	Species eliminated	% Solid residue
Cr(C ₃₉ H ₃₃ O ₆ N ₃)	298-502	13.04	90.21	$3C_2H_6$	9.43 (CrO)
	502-626	15.23	105.35	$NO_2 + C_4H_{11}$	
	626-1141	62.31	431.00	$C_{29}H_4N_2O_3$	
Mo(C ₂₆ H ₂₂ O ₆ N ₂)	365-413	8.50	47.14	C ₃ H ₁₁	23.10 (MoO ₂)
	413–548	17.34	96.13	C_6H_8O	
	548-714	5.41	30.00	NO	
	714-1000	45.67	253.21	$C_{17}H_3 + NO_2$	
$W_2(C_{26}H_{20}O_9N_2)$	323-590	7.68	66.98	C_5H_7	53.11 2(WO ₃)
	590-735	16.60	144.78	$C_6H_{10}O + NO_2$	
	735–965	22.61	197.20	C ₁₅ H ₃ N	
Cr(C ₂₀ H ₁₆ N ₂ O ₃)	323-603	15.62	60.03	2NO	13.53 (Cr)
	603-703	70.87	272.40	$C_{20}H_{16}O$	
Mo ₂ (C ₄₀ H ₃₂ O ₁₀ N ₄)	348-713	30.99	285.27	$C_{15}H_{13} + 2NO_2$	24.33 2(MoO)
	713–933	28.27	260.24	$C_{13}H_{12} + 2NO_2$	
	933-1073	16.42	151.19	$C_{12}H_{7}$	
W ₂ (C ₂₀ H ₁₆ N ₂ O ₈)	328-693	14.37	112.10	$C_5H_6 + NO_2$	55.34 2(WO ₂)
	693-833	7.06	55.10	C_4H_7	
	833–1073	23.22	181.15	$C_{11}H_3 + NO_2$	

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