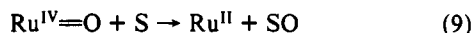
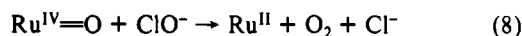
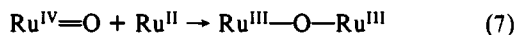
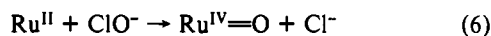


for *trans*-[RuCl₂(DPP)₂], and red for [RuCl(DPP)₂]PF₆, quantitative spectral measurements of the organic phases were prevented by the fact that, as soon as stirring was stopped, the CH₂Cl₂ solutions turned dark green the change being particularly sharp and fast for *cis*-{RuCl₂[(CH₃)₂SO]₄}. On stirring, the organic phases revert again to the initial colors. In some cases, green products could be isolated in the solid state and satisfactorily characterized as oxo-bridged binuclear complexes of ruthenium(III).¹⁷ The green solutions can be therefore considered a sort of "resting" situation, and indeed, they do not exhibit any absorption in the 780–900-cm⁻¹ region, where $\nu(\text{Ru}=\text{O})$ are expected to fall.¹⁸ It is concluded that the following reactions (eqs 6–9)



are likely to take place when aqueous hypochlorite is allowed to be in contact with the organic phase containing the substrate S and the ruthenium(II) complexes. When the contact between the two phases is interrupted, the putative oxoruthenium(IV) intermediate is consumed with final formation of oxo-bridged species,

likely catalytically inactive. With excess hypochlorite, the oxo terminal species is re-formed and, as a consequence, oxidations of both the substrate and the oxidant are allowed to continue.

All the catalysts examined in this investigation exhibit closely related activities and very similar chemoselectivities, despite the significant differences in the chemical environment and stereochemistry. It is therefore possible that a common and very active species is formed in small amounts by the action of hypochlorite on the various complexes since the onset of the reaction. We believe, however, that the active catalysts should be definite complexes of the metal, since the only common species reasonably deriving from the oxidation of the starting complexes are in fact simple "naked" ruthenium oxides, such as RuO₂, and for the latter very different selectivities in the oxygenations of ethers have been reported.^{2a,b} The somewhat higher reactivity exhibited by *cis*-{RuCl₂[(CH₃)₂SO]₄} can be attributed to its solubility in water, where it is present as the aquo derivative {RuCl₂[(CH₃)₂SO]₃·(H₂O)}.¹⁹

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Molecular Vapor Synthesis: The Use of Titanium Monoxide and Vanadium Monoxide Vapors as Reagents

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The production and reactivity of titanium monoxide (TiO) and vanadium monoxide (VO) on a synthetically useful scale were studied by using the techniques and apparatus previously developed for reactions of metal atoms. Cocondensation reactions with chlorine showed that greater amounts of metal atoms were produced as impurities in the vapor when stoichiometric metal monoxides were used as vapor sources than when metal sesquioxides were used. It was found that evaporation of MO and M₂O₃ solids from open tungsten boats yielded vapor compositions of M, MO, and MO₂ similar to those reported earlier from Knudsen cells in the case of vanadium but somewhat different in the case of titanium. The monoxide molecules reacted with chlorine to produce oxometal chlorides in high yields. They reacted with 2,4-pentanedione and other organics containing relatively acidic hydrogen, to form water as a byproduct via protonation of the oxo moiety; coordination compounds of titanium and vanadium were isolated as acac complexes in high yields.

Introduction

In recent years, metal vapor chemistry investigators have explored the use of atomic vapors as synthetic reagents.^{1,2} The same basic techniques and apparatus have been applied to the study of other highly reactive short-lived molecular species including CS,³ BF,⁴ SiX₂,⁵ SiF₃,⁶ SiO,⁷ and others.¹ In an attempt to further expand the number of reactive molecular vapor reagents available,

this work was undertaken as a systematic investigation of the generation and synthetic usefulness of titanium monoxide (TiO) and vanadium monoxide (VO) molecular vapor.

Only two reports have appeared that are concerned with transition-metal oxide vapors as synthetic chemical reagents in low-temperature matrices. Cook and Timms⁸ studied the reactivity of molybdenum and tungsten trioxide vapors, which consist mainly of cyclic trimers along with lesser amounts of dimers, tetramers, and pentamers.¹ Cocondensation of 2,4-pentanedione with MoO₃ vapor followed by warming to room temperature produced a green solid that analyzed as MoO₂(O₂C₅H₇)₂. Presumably 1 molar equiv of water was also formed as a byproduct although no mention was made of its presence. With WO₃ vapor, no reactions occurred with pentanedione if care to avoid ligand pyrolysis was taken. Reactions with methanol, boron trichloride, and other reagents were also described. In general, Cook and Timms concluded that

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metal oxide oligomerization competed favorably with desired reactions, and polymeric mixtures were often formed.

An additional report by Green and co-workers⁹ described the activity of catalysts produced by condensing TiO₂ vapor with Et₂AlCl/toluene/butadiene mixtures. No titanium products were characterized, and the exact nature of the intermediate catalytic species is unknown.

A. The TiO System. The titanium–oxygen system is one of the most complex binary systems known.¹⁰ Solid oxide compounds exist over the range Ti₂O to TiO₂ and the same oxide can exhibit multiple phases.

Several investigations of TiO, TiO₂, and Ti₂O₃ evaporation has been reported.^{11–23} Disagreement about what was the congruently evaporating phase was extant in these reports. The work did lead to a good value for the dissociation energy for TiO equal to 156.9 ± 2.2 kcal/mol or 6.80 ± 0.10 eV.^{15–17} And from these results, Hampson and Gilles¹⁷ pointed out that Ti₂O₃ should produce the maximum amount, though not the maximum pressure, of TiO vapor. Further, more recent work by Granier and Gilles¹⁸ showed that evaporation of TiO solid would lead to a significant vapor pressure of Ti atoms mixed with TiO vapor.

B. The VO System. Vanadium monoxide solid exists in the NaCl crystal structure over a wide oxygen content range VO_{0.75} to VO_{1.20}. It is reportedly unstable above 950 °C in vacuo, where it decomposes into vanadium metal and vanadium sesquioxide. Vanadium sesquioxide, V₂O₃, exists over a very narrow range of homogeneity with a corundum structure having a melting point of 1970 °C.

In addition to V, VO, and VO₂ vapor species, some vanadium oxide solids produce telomeric materials.^{24,25} Thus, Berkowitz and co-workers²⁵ observed V₄O₁₀ and V₄O₈ as well as V₂O₄, V₆O₁₄, and V₆O₁₂ from vaporizing V₂O₅. When a sample of VO solid was vaporized, only V, VO, and VO₂ were observed. Frantseva and Semenov²⁶ found that V₂O₃ was the only congruently vaporizing vanadium oxide^{27,28} and that VO₂ decomposed rapidly to V₂O₃ with the initial evolution of VO₂ vapor.

Results

A. Chlorine Reactions. We evaporated titanium and vanadium oxides (usually 0.1–0.5 g) from tungsten boats under vacuum. Reactions of the vapors with chlorine were used as a chemical method to determine the relative amounts of the vapor species produced. Numerous control experiments were carried out to be certain that solid metal oxides did not react with chlorine to yield products and to ensure that chlorine reactions were not secondarily influencing M, MO, and MO₂ ratios. Likewise, the products of metal vapor (not metal oxide vapor) reactions with chlorine were

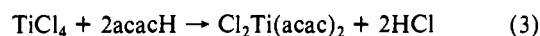
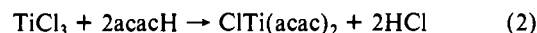
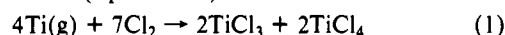
Table I. Relative Proportions of Vapor Species Produced upon Evaporation of Titanium Oxides (Based upon Chlorine Reactions followed by Ligand Trapping)

solid evaporated	% in vapor found ^d (expected) ^e		
	Ti	TiO	TiO ₂
Ti metal ^a	100 (100)	... (...)	... (...)
TiO ^b	46 (77)	54 (23)	... (...)
Ti ₂ O ₃ ^c	trace (0)	73 (...)	27 (...) ^f
Ti ₃ O ₅	... (0)	... (37)	... (63)

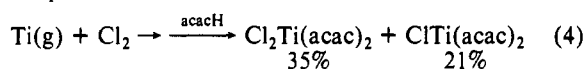
^a Evaporated from a 0.010-in. tungsten boat with resistive heating at 1 × 10⁻⁴ Torr. ^b Evaporated from a 0.005-in. tungsten boat with resistive heating at 1 × 10⁻⁴ Torr. Molten TiO is a golden liquid at evaporation conditions. ^c Evaporated from a 0.005-in. tungsten boat with resistive heating at 1 × 10⁻⁴ Torr. ^d Some losses of vapor occur due to blockage by electrode supports and deposition outside the reaction zone. We assume that Ti atoms react with chlorine to quantitatively give TiCl₃ + TiCl₄. Our isolated yields of TiCl₃ and TiCl₄ totaled 56%. Therefore, we normalized all values for Ti, TiO, and TiO₂ in the vapor accordingly. ^e From refs 17 and 20. ^f Assumed to be about 27%, since good quantitative determinations were not possible.

determined. Thus, titanium atoms and Cl₂ produced a mixture of TiCl₃ and TiCl₄. Since TiCl₄ is volatile and TiCl₃ forms a nonvolatile solid, the two were easily separated from each other and from excess Cl₂ (by trap to trap distillation).

As a means of quantitatively identifying the titanium chloride products, they were separated and allowed to react with 2,4-pentanedione to produce pentanedione products that could be more easily handled (eqs 2 and 3).^{29,30}



The overall reactions and yields (based on metal evaporated) are given in eq 4, for the cocondensation of titanium vapor with chlorine at -196 °C and then trapping with 2,4-pentanedione at room temperature.



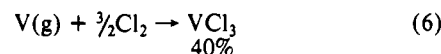
The reactions of TiO molecules with chlorine yielded products shown in eq 5. The Cl₂TiO product was isolated and charac-



terized as OTiCl₂(CH₃CN)₂, a known compound.³¹ However, ClTiO is an insoluble, unreactive solid, which could be separated from the OTiCl₂(CH₃CN)₂ and weighed, along with TiO₂, which was present. Attempts to quantitatively identify TiO in the vapor by reaction with chlorine and subsequent reaction of Cl₂TiO with 2,4-pentanedione produced uncharacterizable products and a higher than expected yield of ClTiO. Therefore, it was difficult to quantitatively determine TiO vs TiO₂ in the vapor.

Using these methods, we were able to determine the relative amounts of Ti and a lower limit of TiO vapors formed from evaporation of titanium oxides, and the results are shown in Table I along with the expected amounts of vapor species based on earlier Knudsen cell experiments.

Analogous vanadium oxide evaporations were easier to deal with, since only one vanadium chloride was produced from the reaction of vanadium atoms with chlorine, and the yield shown is based on metal evaporated (eq 6). The VCl₃ was isolated and



identified by reaction with 2,4-pentanedione according to eq 7.



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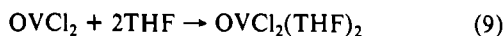
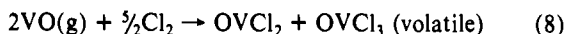
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Table II. Relative Proportions of Vapor Species Produced upon Evaporation of Vanadium Oxides (Based upon Chlorine Reactions followed by Ligand Trapping)

solid evaporated	% in vapor found ^d (expected) ^e		
	V	VO	VO ₂
V metal ^a	100 (100)	... (...)	... (...)
VO ^{b,f}	20 (30)	80 (70)	... (...)
V ₂ O ₃ ^c	2.3 (...)	65 (...)	33 (...)

^a Evaporated from a 0.010-in. tungsten boat with resistive heating at 1×10^{-4} Torr. ^b Evaporated from a 0.005-in. tungsten boat with resistive heating at 1×10^{-4} Torr. ^c Evaporated from a 0.005-in. tungsten boat with resistive heating at 1×10^{-4} Torr. ^d Normalized as described in Table I, assuming 44% loss of vanadium species. ^e From ref 12. ^f Assumed to be about 13%, as good quantitation was not possible. ^g The actual yields in this case were 9% V(acac)₃, due to V atoms, and 50% OV(acac)₂ and 11% OVCl(acac)₂, both due to VO vapor. These combined yields are 70%, somewhat higher than the ~55–60% usually encountered. Therefore, these are simply normalized to the observed yields based on VO solid evaporated.

In an analogous fashion, VO vapor reacted with chlorine to produce oxovanadium dichloride and oxovanadium trichloride. Both of these products were isolated and identified, the OVCl₃ as a pure volatile liquid and the dichloro compound as OVCl₂(THF)₂ (eqs 8 and 9). These compounds, OVCl₂ and OVCl₃,



were also isolated and identified by reaction with 2,4-pentanedione to produce derivatives according to eqs 10 and 11.

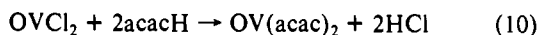
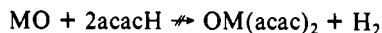
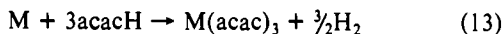
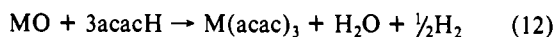


Table II summarizes the percent yields of V, VO, and VO₂ vapor species generated by evaporation of V metal, VO solid, and V₂O₃ solid.

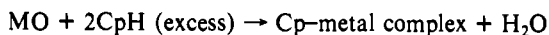
B. 2,4-Pentanedione and Cyclopentadiene Reactions. The direct reaction of 2,4-pentanedione (acacH) with the metal oxide vapors did not produce the expected oxometal (acac) derivatives (M = Ti, V):



Instead, the main products were M(acac)₃ compounds. The observation of water as a byproduct and the insensitivity of the yield to the vapor source (Table III) support eq 12 as the main pathway for MO and eq 13 as the main pathway for M atoms.



Cyclopentadiene also reacted with TiO and VO to yield water plus cyclopentadienyl metal complexes:



When fluorene was codeposited, water was not a byproduct and no organometallic compounds could be isolated.

C. Other Attempted Reactions. Many attempts were made to trap TiO and VO directly as low-valent oxometal adducts. However, no stable products were produced. Thus, 2,2'-bipyridine, tetramethylthiuram disulfide, benzil, pyridine, triethylphosphine, and triethyl phosphite yielded only starting materials.

Similarly, many oxidative addition reactions were attempted which, except for those involving chlorine, proved fruitless. Products of metal atoms were isolated, which will be discussed elsewhere, but no products due to TiO or VO were found. The following substrates were investigated: benzaldehyde, fluorene, trimethylsilane, perfluoro-1-bromo-*n*-octane, chloropentafluoroethane, bromopentafluorobenzene, hexafluoro-2-butyne, and 1-bromo-*n*-butane. Reactions with acidic materials such as methanol and trifluoroacetic acid produced methoxy and trifluoroacetyl

Table III. Yields of OM(acac)₂ and M(acac)₃ for Reaction of MO Vapors with 2,4-Pentanedione Compared with Expected Yield of Metal Atoms from Various Vapor Sources

solid evaporated	% yield ^a		expected % yield of atoms ^b
	OM(acac) ₂	M(acac) ₃	
TiO	none	32	25
Ti ₂ O ₃	2.4	38	trace
VO	none	22	14
V ₂ O ₃	4.1	23	1.3

^a Actual yields based on sample weight vaporized (not normalized). ^b Our work based on Cl₂ reactions (not normalized).

complexes with water and hydrogen as byproducts.

Discussion

Literature reports on the vaporization of titanium and vanadium oxides were all based on evaporations from Knudsen cells, where thermal equilibrium is operable. It is not necessarily expected that evaporation from open boats, where thermal equilibrium of vapor and solid would not be operable, would yield the same relative concentration of M, MO, and MO₂ vapor species. (Actually, there are no reports to our knowledge, where direct comparisons have been made.)

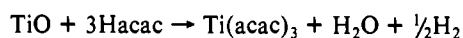
In fact, our results on the relative amounts of T, TiO, and TiO₂ species from TiO and Ti₂O₃ solids do not agree well with the Knudsen cell studies. Thus, Heideman and co-workers²⁰ found about 77% of the vapor above solid TiO was due to Ti atoms, the remainder of which was due to TiO molecules. For the more oxygen-rich sample, Ti₂O₃, Hampson and Gilles¹⁷ found 37% TiO and 63% TiO₂, with no significant amount of Ti atomic vapor. Our results showed about 46% of the vapor from hot TiO was in the form of Ti atoms (Table I) which is considerably lower than the 77% reported by Heideman and co-workers.²⁰

The VO system is not as well studied in this respect. Berkowitz and co-workers¹² found that the ratio of V⁺:VO⁺:VO₂⁺ was 33:76:1 upon mass spectral investigations of VO evaporation from a Knudsen cell at 1672 °C. Our results are in better agreement in the VO case, where about 20% of the vapor is made up of V atoms (Table II).

Since large amounts of Ti and V atoms interfere with the study of TiO and VO as synthons, we investigated Ti₂O₃ and V₂O₃ as sources of the MO species. Tables I and II show our results, based on Cl₂ trapping experiments. Only trace amounts of Ti and V atoms were generated in these cases, and the majority of the vapor was in the form of TiO (73%) and VO (65%). It can be concluded that the sesquioxides are indeed better sources of TiO and VO than the analogous metal monoxide solids. Since the sesquioxides yield very low portions of metal atoms, and since the other products, TiO₂ and VO₂ molecules, should be relatively unreactive, Ti₂O₃ and V₂O₃ solids are usable as TiO and VO vapor sources.

The pentanedione reactions with TiO and VO vapors are summarized in Table III. Surprisingly, metal atoms and MO molecules interact with pentanedione to yield M(acac)₃ complexes. The facile loss of the oxo moiety is intriguing, considering the fact that Ti=O and V=O bonds are quite strong. Formation of water and the addition of a third acac ligand apparently easily overcome the thermodynamic barriers involved.

For the balanced equation which follows, reasonable estimates of bond energies³² of reactants and products show that the reaction is indeed slightly exothermic by about 55 kJ.

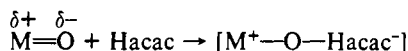


Considering the polar nature of the M=O moiety, and the finding that only relatively acidic C—H bonds react such as in

(32) Using $D_{\text{Ti-O}} = 657 \text{ kJ}$,^{15,16} $D_{\text{C-H(acac)}} = 380 \text{ kJ}$, $D_{\text{Ti-C(acac)}} = 210 \text{ kJ}$, $D_{\text{H-O}} = 497 \text{ kJ}$, and $D_{\text{H-H}} = 435 \text{ kJ}$.³³

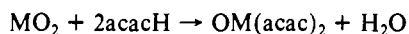
(33) *CRC Handbook of Chemistry and Physics*, 65th ed.; CRC Publishers: Boca Raton, FL, 1984–1985; pp F-182 and F-190. The $D_{\text{C-H(acac)}}$ is estimated on the basis of values reported for similar organic compounds. Likewise, the $D_{\text{Ti-C(acac)}}$ value is an educated guess based on other $D_{\text{M-C}}$ values given.

2,4-pentanedione ($pK_a = 9$) and cyclopentadiene ($pK_a = 15$), it seems likely that the reaction proceeds by protonation as the first step:



Other acidic materials reacted similarly, such as alcohols and carboxylic acids.

The small yields of $\text{OM}(\text{acac})_2$ compounds produced (Table III) from the sesquioxide vaporization studies are probably due to reaction with MO_2 vapor species in similar oxo-protonation reactions:



To our disappointment, TiO and VO vapors did not yield stable low-valent adducts with amines, phosphines, or other similar ligands. Apparently complexes such as $(\text{bpy})_2\text{TiO}$ or $[(\text{EtO})_3\text{P}]_4\text{VO}$ are not stable under our experimental conditions.

Experimental Section

A. General Procedures. All of the cocondensation reactions were carried out by using a standard resistive heating metal atom apparatus.³⁴ Metal oxides were vaporized from 0.005 in. thick tungsten boat sources available from R. D. Mathis Co. The TiO and VO solids were obtained from Cerac Chemical Co. and were 99.9% and 99.5% pure, respectively. The Ti_2O_3 solid used was 99+% from Alfa, and the V_2O_3 was 99% from Aldrich Chemicals. Metals were vaporized from 0.010 in. thick tungsten boats as follows: Granular vanadium (Alfa Chemicals) was heated to its softening point and held there during evaporation. Titanium ($1/8$ -in. rod (Materials Research Corp., Marz grade)) was heated to just below its melting point to avoid alloying with the boat (alloying causes the boat to melt). Manipulations of the compounds were all carried out under anaerobic conditions using standard Schlenkware and a Vacuum Atmospheres drybox.

Chlorine from Matheson was frozen in a liquid-nitrogen trap (evacuated to $<1 \mu\text{m}$) and then expanded into a 3.5-L glass bulb monitoring the pressure via an oil-covered Hg manometer. The bulb was filled to about 500 mmHg prior to reactions, providing a 100-mmol sample that was inlet to the reactor by using a Teflon needle valve and an oil filled bubbler to control the rate. The 2,4-pentanedione (reagent grade) was dried over sodium 2,4-pentanedionate for 24 h and then distilled in vacuo. All solvents (reagent grade) were refluxed under nitrogen and distilled immediately prior to use from appropriate drying agents.

B. Reaction of Metal Oxide Vapors with Chlorine: V_2O_3 Evaporation as a Typical Example. Chlorine (102 mmol) was cocondensed at liquid-nitrogen temperature with 0.089 g (1.31 mmol) of vapor from solid V_2O_3 during a 1-h reaction, forming a yellow-green matrix. As the

reactor warmed, the excess chlorine was pumped out through a -78°C trap, to collect any volatile vanadium-containing compounds, and condensed in a liquid nitrogen trap. After the system was warmed to room temperature, there was a small amount of yellow liquid in the -78°C trap and a light green solid remained in the reactor. The reactor was flushed with N_2 , and the green solid was washed twice with 40 mL of THF and filtered through a fine-porosity fritted-glass disk. The THF solution was reduced to the white solid $\text{OVCl}_2(\text{THF})_2$ in vacuo, and characterized by its mass spectrum and infrared spectrum. The liquid recovered from the -78°C trap was shown to be OVCl_3 by its infrared spectrum and mass spectrum.

C. Reaction of Metal Oxide Vapors and 2,4-Pentanedione: TiO Evaporation as a Typical Example. During a 2-h reaction about 30 mL of 2,4-pentanedione was codeposited with 0.293 g (4.57 mmol, 42% of the sample) of vapor from TiO. The matrix varied in color from light brown to brown-black immediately after the Dewar flask was removed. The matrix turned blue upon warming. Excess 2,4-pentanedione was recovered, leaving a dark blue solid. The reactor was flushed with N_2 , the contents were washed out with 50 mL of toluene, and the mixture was filtered. The toluene was evaporated, leaving 0.498 g (31.6% yield) of $\text{Ti}(\text{acac})_3$, identified by comparison of its mass spectrum and infrared spectrum with those of a sample from Aldrich. The recovered excess 2,4-pentanedione contained a few drops of immiscible liquid identified as water by GC/MS.

D. Analysis of $\text{OV}(\text{acac})_2$ and $\text{V}(\text{acac})_3$ Mixtures. Quantitative Mass Spectral Analysis. Three standard samples of $\text{OV}(\text{acac})_2$ and $\text{V}(\text{acac})_3$ containing 41.5, 8.46, and 4.44 mol % $\text{V}(\text{acac})_3$ were prepared in a N_2 -filled glovebox and intimately ground. Approximately 1-mg samples of the standards were quantitatively vaporized in the mass spectrometer by slowly heating the probe to 250°C at $15^\circ\text{C}/\text{min}$ while one scan/3 s was acquired for 20 min at 15 eV. Individual mass chromatograms were generated for the 265- and 348-amu ion intensity. These showed that $\text{V}(\text{acac})_3$ vaporized at a slightly lower temperature range of 50 – 150°C , while $\text{OV}(\text{acac})_2$ vaporized from 100 to 200°C . At 225°C the intensity of both ions had reduced and leveled off. Integration of the parent ion peak intensity of the $\text{OV}(\text{acac})_2$ (265 amu) and the $\text{V}(\text{acac})_3$ compound (348 amu) versus time gave 40.2, 7.87, and 4.72 mol % $\text{V}(\text{acac})_3$. The method was therefore shown to be valid to within ± 1.5 mol % and was used to calculate the percent composition of the compound mixture obtained from the reaction of 2,4-pentanedione with metal oxides and the metal chloride compounds.

Qualitative Infrared Spectral Analysis. The infrared spectra of pure samples obtained from Aldrich Chemical Co. were recorded for the purpose of comparison with product mixtures obtained. All sample spectra were obtained as Nujol mulls prepared in a nitrogen-filled glovebox and placed between two KBr plates.

For the titanium compounds the most obvious difference in the spectra is the appearance of a band at 590 cm^{-1} , which can be attributed to the bridging oxo group.

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Chemistry of Perfluoromethylsulfonyl Perfluorobutylsulfonyl Imide

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Selected chemistry of the unsymmetrical imide perfluoromethylsulfonyl perfluorobutylsulfonylimide, $\text{CF}_3\text{SO}_2\text{N}(\text{H})\text{SO}_2\text{C}_4\text{F}_9$, is described. The potassium, cesium, and silver derivatives were prepared by reaction of the respective carbonates with the imide. The silver compound is a useful reagent for synthesis of both organic and inorganic derivatives. Reaction with methyl iodide or ethyl iodide resulted in high yields of the alkyl imides. Chlorine reacts with the silver derivative to give the chloroimide in excellent yield. Reaction of $\text{CF}_3\text{SO}_2\text{N}(\text{Cl})\text{SO}_2\text{C}_4\text{F}_9$ with NO and NO_2 formed the corresponding nitroso and nitro derivatives, and CO and ethylene react at 22°C to give addition compounds. UV photolysis of the chloroimide resulted in the quantitative formation of $\text{C}_4\text{F}_9\text{Cl}$ and the cyclic dimer of the resultant $\text{CF}_3\text{SO}_2\text{NSO}_2$.

Introduction

The (trifluoromethyl)sulfonyl group, CF_3SO_2 -, has been reported to be one of the strongest neutral electron-withdrawing groups.^{1,2} Furthermore, the CF_3SO_2 - group has the added

synthetic value of having high stability under a wide variety of reaction conditions.³⁻⁵ In disubstituted amines, the presence of

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