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INTERACTION OF THIIRENE 1,1-DIOXIDES WITH TRANSITION METAL COMPLEXES

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SUMMARY

The decomposition of thiirene 1,1-dioxides into sulphur dioxide and the corresponding acetylenes is catalysed by certain transition metal complexes [Pd^0, Pt^0 and Ir^I]. The metal complexes of the substrate are key intermediates in the decomposition. A possible pathway is suggested.

INTRODUCTION

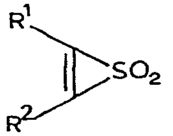
As part of our investigation into the change in chemical reactivity of an olefinic system brought about by coordination to a transition metal complex, we have already studied some zerovalent platinum cyclopropene complexes[1]. One of the most striking results was that these complexes are thermally very stable relative to the unsaturated hydrocarbons themselves.

We now report on the coordination of some thiirene 1,1-dioxides[2] with zerovalent metals. Attention is also given to the kinetic and mechanistic aspects of both the thermal and the catalysed decomposition, and in particular the role of the metal. Preliminary results of this work have appeared elsewhere[3].

RESULTS AND DISCUSSION

Transition metal complexes of thiirene 1,1-*dioxides*

Zerovalent platinum and palladium complexes of the thiirene 1,1-dioxides (I)–(IV) were prepared by ligand exchange with L_2PtX (L = triphenylphosphine,



(I), $R^1 = H, R^2 = CH_3$
(II), $R^1 = R^2 = CH_3$
(III), $R^1 = CH_3; R^2 = C_6H_5$
(IV), $R^1 = R^2 = C_6H_5$

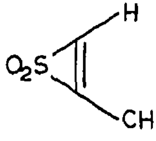
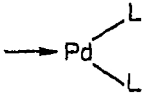
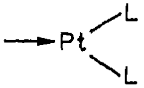
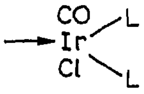
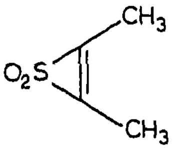
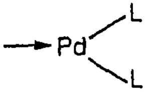
X = triphenylphosphine, ethylene or carbon disulphide) and PdL_4 at ambient temperature, in toluene or chloroform as the solvent. The only compound which coordinated to Vaska's complex [*trans*-$IrL_2(CO)Cl$] was methylthiirene 1,1-dioxide (I).

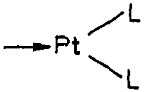
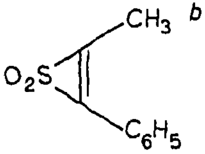
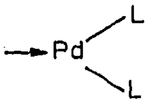
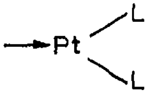
(*continued on* p. 406)

TABLE 1

PMR DATA FOR THIIRENE DIOXIDES AND THEIR COMPLEXES IN $CDCl_3$

Chemical shifts in ppm downfield from TMS (δ); coupling constants in Hz

	H	CH_3	$J(H\text{–}CH_3)$	$J(P\text{–}H)$	$J(P'\text{–}H)$	$J(P\text{–}CH_3)$	$J(P'\text{–}CH_3)$	$J(Pt\text{–}H)^a$	$J(Pt\text{–}CH_3)^a$
 *b*	8.99	2.44	1.1						
 *c*	4.17	1.33	0	10.5	1	7.5	2		
	3.29	1.40	0	7.5	1	7.5	0	25	31
	3.45	1.69	0	5.5	1	7.5	0		
 *b*		2.28							
 *c*		1.17				7.5^d			

	1.11	7.0[d]		29
	2.61			
	1.23	7.0	0	
	1.25	7.5	0	27

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[a] ^{195}Pt present in 33.8% (natural abundance). [b] ref. 2. [c] In the presence of free triphenylphosphine ligand exchange occurs, as was concluded from the disappearance of the P–H coupling. [d] An example of an $A_3XX'A'_3$ system; the reported value is $|J(P\text{–}CH_3)|+|J(P'\text{–}CH_3)|$, see ref. 8.

According to NMR spectroscopy the exchange reactions with the palladium and platinum complexes were complete within a few minutes. Complexes of (I) and (II) were isolated at temperatures below 0°. Attempts to isolate complexes of (III) failed and mixtures containing the complex together with metal sulphate were obtained. With diphenylthiirene 1,1-dioxide (IV) the rate of complex-formation proved to be of the same order of magnitude as the rate of decomposition.

Structural assignments were based on spectroscopic evidence (Table 1). In all complexes, coordination most probably occurred via the carbon–carbon double bond, as was concluded from the following NMR and IR spectroscopic data:

(*i*). The absorption at 1614 cm^{-1} in the C=C stretching frequency region, observed with methylthiirene 1,1-dioxide, was absent in the spectra of its complexes. (Additionally, the signals assigned to SO_2 frequencies, at ca. 1260 and 1170 cm^{-1}, were also shifted on complexation*.)

(*ii*). The allylic H–CH_3 coupling (1.1 Hz) in the NMR spectrum of methylthiirene 1,1-dioxide disappeared on coordination.

(*iii*). The proton chemical shifts and ^{195}Pt–H and P–H coupling constants were similar to those of cyclopropene platinum(0) complexes, whose double-bond coordination has previously been established on the basis of crystal structure[1].

(*iv*). In the palladium and platinum complexes of dimethylthiirene 1,1-dioxide the two methyl groups were magnetically identical, indicating a symmetrical structure.

The metals were found to have a remarkably strong tendency to coordinate with thiirene 1,1-dioxides. Addition of strong coordinating ligands such as 1,2- bis(diphenylphosphino)ethane or tetracyanoethylene to bis(triphenylphosphine)(methylthiirene1,1-dioxide)platinum did not result in noticeable displacement of (I).

The thermal stability of the complexes will be dealt with below.

Decomposition of thiirene 1,1-dioxides

Thiirene 1,1-dioxides (I)–(IV) are known to be stable at temperatures up to about 80–120°, depending on the substituents. At higher temperatures they decompose quantitatively into the corresponding acetylenes and sulphur dioxide; the kinetics of thermal decomposition in solution have been reported by Carpino[2]. Additional data for our model compounds have been determined by NMR spectroscopy (Table 2).

The decomposition of the thiirene 1,1-dioxides was found to be catalysed by certain transition metals, zerovalent palladium and platinum complexes and monovalent rhodium and iridium complexes were active in this respect, whereas divalent platinum and palladium complexes had no effect.

A kinetic study of the decomposition of methylthiirene 1,1-dioxide catalysed by bis(triphenylphosphine)(ethylene)platinum, whose ethylene ligand is quantitatively exchanged for methylthiirene 1,1-dioxide, revealed that the rate of decomposition (measured by NMR spectroscopy) is zero order with respect to thiirene 1,1-

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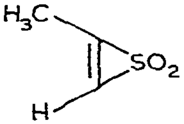
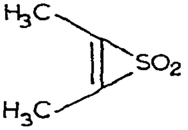
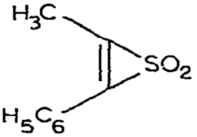
* The IR spectra of the Pd^0 and Pt^0 complexes contained several characteristic bands at 1225–1230, 1118–1130 1040–1050 cm^{-1}, and that of the Ir^I complex of methylthiirene 1,1-dioxide at 1250, 1140 and 1048 cm^{-1}. The spectrum of the reaction mixture of diphenylthiirene 1,1-dioxide and bis(triphenylphosphine)(ethylene)platinum ($CDCl_3$ solution, −25°) featured absorptions at 1215, 1120 and 1020 cm^{-1}.

TABLE 2

RATES OF THERMAL DECOMPOSITION OF THIIRENE 1,1-DIOXIDES (I)–(III)

Compound		*Temp.* (°*C*)	*Rate* ($10^3\,s^{-1}$)
	(I)	104	0.75
		116	1.30
		126	2.69
	(II)	100	0.45
		111	1.58
		120	5.02
	(III)	100	0.54
		111	1.46
		121	2.96

dioxide. In addition, the concentration of the methylthiirene 1,1-dioxide complex remained constant as long as free methylthiirene 1,1-dioxide was present. Thus, this compound coordinates more strongly than sulphur dioxide or propyne with Pt^0. On the basis of these observations we propose the following kinetic schemes*:

$$L_2Pt(TD) \xrightarrow{k_{1a}} L_2Pt(\text{Acetylene}) + SO_2$$

$$TD + L_2Pt(\text{Acetylene}) \underset{k_{-2a}}{\overset{k_{2a}}{\rightleftarrows}} L_2Pt(TD) + \text{Acetylene},$$

or

$$L_2Pt(TD) \xrightarrow{k_{1b}} L_2PtSO_2 + \text{Acetylene}$$

$$TD + L_2PtSO_2 \underset{k_{-2b}}{\overset{k_{2b}}{\rightleftarrows}} L_2Pt(TD) + SO_2$$

Although similar, the two schemes differ in that either sulphur dioxide or acetylene is generated in the decomposition step. Since the exchange processes are fast compared with the rates of decomposition, the rate constant for the decomposition of thiirene 1,1-dioxide can be written as $k_{obs} = k_1 \cdot [Cat]/[TD]$. From kinetic experiments we derived the rate constant k_1 and the activation parameter E_a (18.3 kcal/mol). Additional evidence for the mechanism was provided by the following experimental results. Decomposition of $L_2M(TD)$ at temperatures much lower than those required

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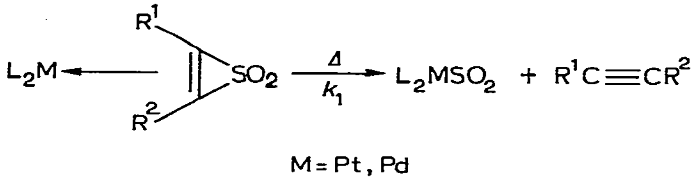
* L = Triphenylphosphine and TD = thiirene 1,1-dioxide.

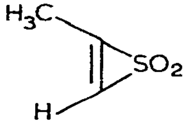
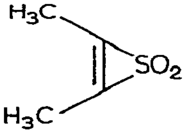
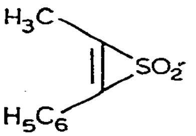
for decomposition of free thiirene 1,1-dioxide also gave rise to the corresponding acetylene and the sulphur dioxide metal complex*.

SCHEME 1



The kinetics of this reaction were measured by NMR spectroscopy in order to quantitatively assess factors influencing the stability of the complexes. The rate constants and the derived activation parameter for the decomposition which is first-order in complex for at least two half-lives, are presented in Table 3.

TABLE 3. RATE CONSTANTS AND ACTIVATION ENERGIES FOR THE DECOMPOSITION OF $L_2Pt(TD)$ AND $L_2Pd(TD)^a$

Compound	*$L_2Pt(TD)$*			*$L_2Pd(TD)$*		
	Rate constant (s^{-1})	*Temp. (°C)*	*E_a (kcal/mol)*	*Rate constant (s^{-1})*	*Temp. (°C)*	*E_a (kcal/mol)*
	1.41×10^{-3}	31	18.3±0.5	0.46×10^{-3}	50	22±2
	2.38×10^{-3}	34		1.52×10^{-3}	60	
	5.70×10^{-3}	48		2.57×10^{-3}	69	
	0.47×10^{-3}	29	19±2	0.58×10^{-3}	50	22±2
	1.66×10^{-3}	39		1.12×10^{-3}	59	
	3.39×10^{-3}	49		3.73×10^{-3}	70	
	1.14×10^{-3}	13	20±2	1.38×10^{-3}	39	23±2
	2.41×10^{-3}	16		1.93×10^{-3}	46	
	5.02×10^{-3}	27		5.25×10^{-3}	55	

[a] TD = thiirene 1,1-dioxide; L = triphenylphosphine.

The values of k_1 of the decomposition of bis(triphenylphosphine)(methylthiirene 1,1-dioxide)platinum exactly fitted the graph of k_1 *vs.* temperature obtained in the kinetic study of the bis(triphenylphosphine)(methylthiirene 1,1-dioxide)-platinum-catalysed decomposition of methylthiirene 1,1-dioxide (Fig. 1).

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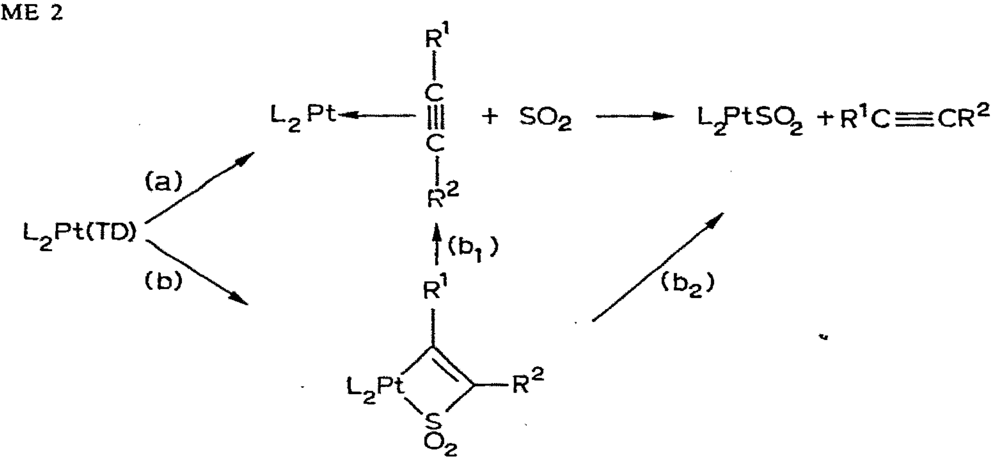
* These complexes were always isolated as L_2MSO_4 owing to rapid oxidation of the sulphur dioxide ligand.

thiirene 1,1-dioxide (Fig. 1).

The difference in stability between methyl- and dimethylthiirene 1,1-dioxide complexes on the one hand and the methylphenyl- and diphenyl-substituted complexes on the other might be related to the fact that decomposition of the phenyl-substituted thiirene 1,1-dioxides is accompanied by release of steric strain (bulky vicinal substituents) and an increase in resonance energy. The decomposition of the complexes may be thought to proceed via two mechanisms:

SCHEME 2



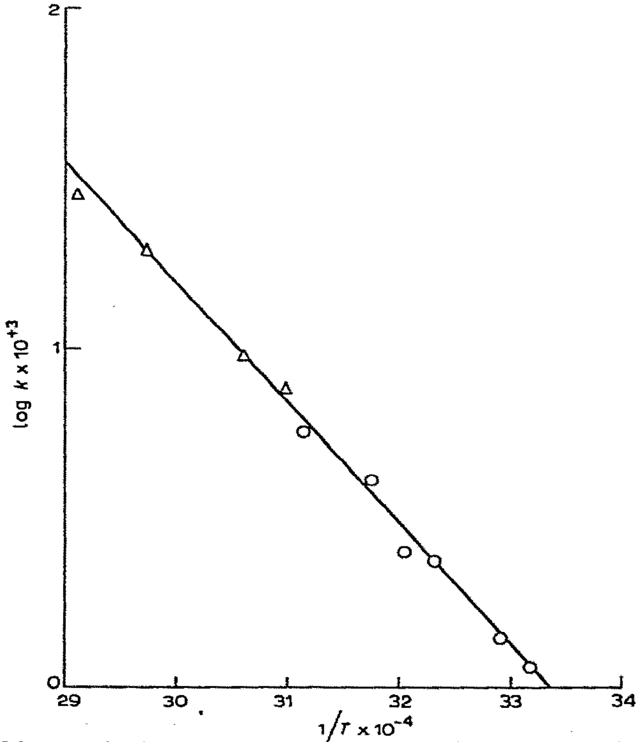


Fig. 1. Arrhenius plot of the rate of decomposition k_1 derived from decomposition of L_2Pt (methylthiirene 1,1-dioxide) (○) and from catalytic decomposition of methylthiirene 1,1-dioxide (△).

Route (a) comprises extrusion of sulphur dioxide (either concerted or non-concerted) with the formation of bis(triphenylphosphine) (propyne)platinum. The two products subsequently enter into an exchange reaction to give free propyne and the sulphur dioxide complex*. Route (b) involves a more active participation of the metal; here the platinum forms a bond to sulphur (or oxygen) and possibly to carbon as well. This results in direct transfer of the sulphone moiety to the metal; subsequent extrusion of sulphur dioxide or propyne from the intermediate (one possible intermediate is drawn in Scheme 2**) proceeds either via route (b_1) or route (b_2). Intermediates such as those generated by route (b) could not be observed by NMR spectroscopy.

In order to differentiate between a mechanism involving direct sulphur dioxide transfer (route b_2) and a mechanism in which the sulphur dioxide is transferred to the metal via the solution [routes (a) and (b_1)], we studied the decomposition of bis(triphenylphosphine) (methylthiirene 1,1-dioxide)platinum in the presence of sulphur dioxide labelled with ^{35}S ($^*SO_2$). The results are given in Table 4. The amount of $^*SO_2$ incorporated during decomposition of the complex cannot be accounted for by assuming an exchange between the sulphur dioxide complex produced and the radioactive $^*SO_2$ in solution. It is larger than $1.70/(1.58+1.70)\times 100=52\%$ (see Table 4), due to the fact that the L_2PtSO_2 initially produced takes up its sulphur dioxide from an $^*SO_2$-enriched solution. The ratio $^*SO_2$/total sulphur dioxide decreases as the reaction proceeds. Consequently, at the end of the reaction the (L_2PtSO_2) complex formed should have a higher $^*SO_2$/total sulphur dioxide ratio than the solution from which it is isolated. Separate experiments revealed that acetylenes do not catalyse such an exchange between L_2PtSO_2 and SO_2 in solution. These results indicate that decomposition proceeds predominantly via route (a) or (b_1).

Comparison of the rates of decomposition of the thiirene 1,1-dioxide complexes with those of thiirene 1,1-dioxides[2] (Table 2) and thiirene 1,1-dioxides[5] shows that the values found for the complexes are similar to those reported for the thiirene 1,1-dioxides (Table 5). Carpino *et al.*[2] have already commented on the difference in thermal stability between thiirene 1,1-dioxides and thiirane 1,1-dioxides. They

TABLE 4

DECOMPOSITION OF L_2Pt(METHYLTHIIRENE 1,1-DIOXIDE) IN THE PRESENCE OF ^{35}S-LABELLED SULPHUR DIOXIDE ($^*SO_2$)

$L_2Pt(I)^a$	$L_2Pt\,SO_2{}^a$	$(I)^a$	$SO_2{}^a$	$^*SO_2{}^a$	$L_2Pt^*SO_2$ (%)
1.17		0.41		1.70	64
	1.03		0.67	1.70	23

[a] Added in this sequence.

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* In separate experiments it was shown that acetylene has far less tendency to coordinate to Pt^0 than sulphur dioxide, which in turn is quantitatively displaced by methylthiirene 1,1-dioxide.

** In the reaction of methylcyclopropenone with bis(triphenylphosphine)(ethylene)platinum, the initially formed olefin complex rearranges to 1,1-bis(triphenylphosphine)-3-methylplatinacyclobut-3-en-2-one; this complex, however, does not decompose to give propyne[4].

TABLE 5

RATES OF EXPULSION OF SULPHUR DIOXIDE FROM VARIOUS COMPOUNDS[a]

Compound	*Temp.* (°C)	$k(s^{-1})$	*Ref.*
Phenylthiirane 1,1-dioxide	25	8×10^{-4}	4
cis-2,3-Diphenylthiirane 1,1-dioxide	25	1.3×10^{-4}	4
trans-2,3-Diphenylthiirane 1,1-dioxide	25	4×10^{-3}	4
Diphenylthiirene 1,1-dioxide	75	0.68×10^{-4}	2
Dimethylthiirene 1,1-dioxide	75	0.58×10^{-4}	2
L_2Pt(Dimethylthiirene 1,1-dioxide)	25	3.4×10^{-4}	
L_2Pt(Methylphenylthiirene 1,1-dioxide)	25	1.5×10^{-3}	
L_2Pd(Methylphenylthiirene 1,1-dioxide)	25	1.5×10^{-4}	

[a] In $CHCl_3$ or $CDCl_3$.

associated the high stability of the former with the possibility of delocalization of the π-electrons of the double bond via the empty *d*-orbitals of the sulphone group.

The similarity between the rates of decomposition of the thiirene 1,1-dioxide complexes and those of the thiirane 1,1-dioxides is attributed to the fact that upon coordination the carbon–carbon bond order of the thiirene 1,1-dioxides decreases and the ligand becomes thiirane 1,1-dioxide-like*. The catalytic role of the metal consists in saturating the carbon–carbon double bond, resulting in a lower stability of the thiirene 1,1-dioxide ligand. We are thus tempted to conclude that thermal decomposition of bis(triphenylphosphine)(methylthiirene 1,1-dioxide)platinum proceeds via route (a).

This mechanism also explains why the palladium complexes are more stable than the platinum complexes. The coordinating ability of the d^{10} metals is related to the $(n-1)d^{10} \rightarrow (n-1)d^9\,np$ promotion energy[6]; this energy is higher for Pd (4.23 eV) than for Pt (3.28 eV)[7]. Therefore, it is expected that thiirene 1,1-dioxides coordinate more strongly to Pt^0 than to Pd^0. The bond order of the coordinated double bond decreases to a larger extent in the Pt^0 complexes than in the Pd^0 complexes, resulting in a lower stability of the former.

CONCLUSIONS

Catalytic amounts of low valency transition metal complexes catalyse the decomposition of thiirene 1,1-dioxides into acetylenes and sulphur dioxide. A detailed mechanistic study has revealed that the decomposition proceeds via a thiirene 1,1-dioxide–metal complex as the key intermediate. The metal acts as an electron donor, decreasing the bond order of the double bonds of the thiirene 1,1-dioxides in their complexes. As a result, the reactivity of the coordinated thiirene 1,1-dioxide approaches that of thiirane 1,1-dioxide, which is known to be thermally less stable than its unsaturated counterpart.

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* The Pt^0 complex of thiete 1,1-dioxide is thermally as stable as the corresponding thietane 1,1-dioxide. This complex was prepared in the same way as those of the methylthiirene 1,1-dioxides, *viz.* by ligand exchange with $L_2Pt(C_2H_4)$. Its structure was shown to be of the same type (PMR spectrum: 4 protons at 2.64, 3.59, 4.01 and 4.44 ppm, all having Pt satellites.

EXPERIMENTAL

NMR and IR spectra were recorded on Varian HA-100 and Perkin-Elmer 457 spectrometers respectively.

Thiirene 1,1-dioxides (I)–(IV) were prepared by literature procedures[2].

General procedure for the preparation of complexes of (di)methylthiirene 1,1-*dioxides*

A solution of the thiirene 1,1-dioxide in chloroform or toluene was added to an equimolar amount of $L_2Pt(C_2H_4)$, PdL_4, PtL_4 or $L_2Ir(CO)Cl$* dissolved or suspended in the same solvent. After completion of the reaction, ether or ethanol was added and the crystalline complex filtered off (yields 50–80%). The complexes were not recrystallized in view of their thermal instability. Their elemental analyses are given in Table 6.

TABLE 6

ELEMENTAL ANALYSES OF THE COMPLEXES

Structure	*Found (%)*			*Calcd. (%)*		
	C	*H*	*S*	*C*	*H*	*S*
$L_2Pt(I)^a$	56.6	4.1	4.1	56.86	4.16	3.89
$L_2Ir(CO)(Cl)(I)$	52.7	3.9	3.1	54.33	3.87	3.63
$L_2Pd(I)$	62.8	4.6	4.6	63.72	4.66	4.36
$L_2Pt(II)$	56.4	4.4	4.1	57.32	4.33	3.83
$L_2Pd(II)$	62.9	4.9	4.1	64.14	4.84	4.28

[a] L = triphenylphosphine; (I), (II) see p. 403.

Solutions for NMR and IR spectroscopy were prepared by adding the thiirene 1,1-dioxide (I)–(IV) to a solution or suspension of an equimolar amount of the complex.

Labelling experiments

Quantities (20–25 μl) of stock solutions of $^*SO_2$ and SO_2 in toluene were added to cooled solutions of the complexes in 20 ml of chloroform. After reaction for 30 min at 42° the greater part of the solvent was evaporated *in vacuo* and the $L_2PtSO_2 + L_2PtSO_4$ mixtures were isolated in 50–80% yield. These samples were dissolved in a mixture of water (2 ml), dioxane (4 ml) and Instagel** containing 2,5-diphenyloxazole and 2,2'-*p*-phenylenebis(4-methyl-5-phenyloxazole) as scintillators. The radioactivity of these solutions was determined with a Packard Tricarb model 3003 scintillation-counter.

The efficiency of the counting was determined subsequently by adding 25 μl of toluene-7-^{14}C as internal standard to the counted solution. The number of counts was sufficient to attain 1% accuracy.

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* Only for methylthiirene 1,1-dioxide.

** Packard Instruments Company, Inc.

Kinetics of the thermal decomposition of thiirene 1,1-*dioxides and their* Pd^0 *and* Pt^0 *complexes*

(*a*). *Thiirene* 1,1-*dioxides*. The thiirene 1,1-dioxide (0.2 mmol) was dissolved in 0.2 ml of pentachloroethane and the rate of decomposition was determined by measuring the intensity of the signals corresponding to the methyl group(s) in (I)–(III) as a function of time by PMR spectroscopy (hexamethyldisilane as external reference). The decomposition was first order for at least two half-lives in all cases. The exact temperatures were determined from the methanol shift $[\Delta(\delta_{CH_3}-\delta_{OH})]$-temperature relation. Results are given in Table 2.

(*b*). Pd^0 *and* Pt^0 *complexes of thiirene* 1,1-*dioxide*. The Pd^0 and Pt^0 complexes of thiirene 1,1-dioxides (I)–(III) were prepared by ligand exchange (−20° to 0°) in deuterochloroform. Their rates of decomposition were measured as described above (*a*) (tetramethylsilane as external reference). Results are given in Table 3.

(*c*). *Catalytic experiments*. The rate of decomposition of a mixture of thiirene 1,1-dioxide and the corresponding metal complex (1–5 %) was measured as described in section (*a*) above (dichloromethane as external reference). The decomposition was zero-order for more than two half-lives. The results are given in Table 3.

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