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used to describe the reaction.^{19,20} If the interactions are weak an equation of the form:

$$\Delta G^* = 0.50E^0 + W$$

has been used²⁰ where ΔG^* is the free energy of activation for the reaction, E^0 is the redox potential of the organic substrate, and W is a term which involves the redox potential of the metal ion, the equilibrium constant, and the electron-exchange rates of the half-reactions. Use of the present data, however, for the reactions which involve both the metal ion and the hydroxy-species, gave marked curvature in the ΔG^* vs. E^0 plots. In four out of the five cases where there is no adherence to a Marcus treatment of this type one of the reacting

¹⁹ G. Dulz and N. Sutin, *Inorg. Chem.*, 1963, **2**, 917.

²⁰ H. Diebler and N. Sutin, *J. Phys. Chem.*, 1964, **68**, 174.

species is a cobaltic ion.^{21,22} Such discrepancies have been explained in terms of reaction *via* an inner-sphere mechanism and in terms of spin multiplicity restrictions.²²

At present there can be no unambiguous decision between the two mechanisms, but the similarity of reaction rates with those where intermediates have been shown to exist would tend to suggest the inner-sphere route.

We thank the Nigerian Government for a grant (to U. D. G.) and the Royal Society for a grant-in-aid towards part of the apparatus.

[8/1613 Received, November 11th, 1968]

²¹ N. Sutin, *Ann. Rev. Phys. Chem.*, 1966, **17**, 119.

²² J. C. Sullivan and R. C. Thomson, *Inorg. Chem.*, 1967, **6**, 1795.

Metallo-organic Compounds Containing Metal-Nitrogen Bonds. Part VI.¹ Infrared and Nuclear Magnetic Resonance of Dialkylamido-derivatives of Titanium, Vanadium, Zirconium, Niobium, Hafnium, Tantalum, and Thorium

By D. C. Bradley *† and M. H. Gitlitz, Department of Chemistry, The University of Western Ontario, London, Ontario, Canada

I.r. and n.m.r. spectra have been measured on solutions of a number of dialkylamido-compounds $M(NR_2)_x$ of titanium, vanadium, zirconium, niobium, hafnium, tantalum, and thorium and on the alkylimido-trisdialkylamido-tantalums $RN=Ta(NR_2)_3$. Assignments of characteristic bands are made and the metal-nitrogen stretching frequencies are discussed in terms of a significant contribution of nitrogen $\rightarrow$ metal $p_\pi-d_\pi$ bonding. The variable temperature n.m.r. studies on $Zr(NMe_2)_4$ confirmed the presence of polymeric species in solution.

THE dialkylamido-derivatives $M(NR_2)_x$ of titanium,² zirconium,³ niobium,⁴ and tantalum⁵ are highly reactive compounds which are soluble in common organic solvents and can be distilled under reduced pressure. In order to characterize these compounds further and to determine the nature of the covalent metal-nitrogen bond we have measured the i.r. and n.m.r. spectra of a range of these compounds and similar derivatives of vanadium, hafnium, and thorium. We have also investigated further the reactions of tantalum pentachloride and lithium dialkylamides which gave rise to the remarkable alkylimidotrisdialkylamidotantalums $RN=Ta(NR_2)_3$ ⁴ with the aim of characterizing these compounds.

I.r. Spectra.—All the compounds gave a medium-to-strong absorption band in the region 700–500 cm^{-1} which was absent in the parent amine and is accordingly assigned as a predominantly metal-nitrogen stretching mode.⁵ Several other characteristic strong bands involving the ligand were also observed and some tentative assignments are made.

Metal Dimethylamides.—The bands in the 1250–500

cm^{-1} region are listed in Table 1. The tetrakisdimethylamido-derivatives $M(NMe_2)_4$ give the single metal-nitrogen band [asymmetric stretch, ν_3 (F_2)] expected for local T_d symmetry of the MN_4 group. Bürger *et al.*⁶

TABLE 1

Characteristic i.r. (cm^{-1}) in metal dimethylamides

Com- pound †	M–N Stretching	sym. NC_2	CH_3 rocking or asym. NC_2	CH_3 - deform.
Ti(NMe_2) ₄	592s	950vs	1055w 1154s	1250s
Zr(NMe_2) ₄	537s	936vs	1061w 1151s	1246s
Hf(NMe_2) ₄	533s	943vs	1063w 1151s	1253s
V(NMe_2) ₄	595s	944vs	1048m 1147s	1243s
Nb(NMe_2) ₅	540s	938vs	1043m 1143s	1243m
Ta(NMe_2) ₅	528m	943vs	1040m 1155m	1236m

† All spectra in cyclohexane solution.

who determined the i.r. and Raman spectra for $Ti(NMe_2)_4$ showed that the symmetrical TiN_4 stretching frequency [ν_1 , (A_1) Raman-active only] occurred at 532 cm^{-1} . It is noteworthy that, as expected, the asymmetric MN_4 stretching frequencies of the first-row transition

³ D. C. Bradley and I. M. Thomas, *Canad. J. Chem.*, 1962, **40**, 449.

⁴ D. C. Bradley and I. M. Thomas, *Canad. J. Chem.*, 1962, **40**, 1355.

⁵ D. C. Bradley and M. H. Gitlitz, *Nature*, 1968, **218**, 353.

⁶ H. Bürger, H. Stammreich, and Th. T. Sans, *Monatsh. Chem.*, 1966, **97**, 1276.

† Present address: Dept. of Chemistry, Queen Mary College, Mile End, London E.1.

¹ Part V, D. C. Bradley and K. J. Chivers, *J. Chem. Soc. (A)*, 1968, 1967.

² D. C. Bradley and I. M. Thomas, *J. Chem. Soc.*, 1960, 3857.

metals (Ti, V) are considerably higher than those of the second- and third-row elements (Zr, Hf). Although the molecular weight determination showed that $\text{Zr}(\text{NMe}_2)_4$ was not completely monomeric (degree of polymerization = 1.22) and our n.m.r. spectra show evidence for polymerization at low temperatures, the i.r. spectrum showed no bands that could be attributed to bridging dimethylamido-groups. Also the monomeric pentakisdimethylamido-compounds of niobium and tantalum gave only one metal-nitrogen stretching frequency whereas more bands would be expected for a hexatomic grouping MN_5 [e.g. two bands (A''_2 , E') for D_{3h} symmetry and three bands ($2A_1$, E) for C_{4v} symmetry]. On the assumption that the structures are trigonal bipyramidal (D_{3h}) we conclude that the two MN_5 stretching frequencies are too close to be resolved. Interestingly, for both the second-row (Zr, Nb) and third-row (Hf, Ta) pairs of elements the metal-nitrogen stretching frequencies are very close although the quinquivalent species would be expected to exhibit considerably higher frequencies than the quadrivalent species. This might be due to the effect of greater steric strain in the $\text{M}(\text{NMe}_2)_5$ compounds causing weakening of the M-N bonds. Thus, it was found that steric strain was so great for the bulkier ligands (NR_2 where $\text{R} = \text{Et}$, Pr^n , or Bu^n) that $\text{M}(\text{NR}_2)_5$ compounds were unstable and gave rise to $\text{Nb}(\text{NR}_2)_4$ ³ and $\text{RN}=\text{Ta}(\text{NR}_2)_3$ ⁴. All the metal dimethylamides gave an intense band in the range 936–950 cm^{-1} due to the symmetric NC_2 stretching mode which is useful for the identification of MNMe_2 groups. Two other characteristic bands occurred near 1050 and 1150 cm^{-1} and are probably due to methyl-rocking and asymmetric NC_2 modes but further work involving deuteriated derivatives is required to distinguish them; they are probably strongly coupled. Following Bürger *et al.*⁶ the strong band at *ca.* 1250 cm^{-1} is assigned to the methyl deformation mode. However, none of these ligand bands are as sensitive to the nature of the bonded metal as the metal-nitrogen frequency.

Metal Diethylamides.—In Table 2 are listed the metal-nitrogen frequencies and tentative assignment of some

TABLE 2

Characteristic i.r. bands (cm^{-1}) in metal diethylamides

Compound †	M-N Stretching	sym. NC_2	asym. NC_2	Unassigned
$\text{Ti}(\text{NEt}_2)_4$	610s	1003vs	1153m	1185m
$\text{Zr}(\text{NEt}_2)_4$	577m	1000vs	1153s	1184s
$\text{Hf}(\text{NEt}_2)_4$	577m	1002vs	1158s	1187s
$\text{V}(\text{NEt}_2)_4$	613s	1001vs	1152s	1182s
$\text{Nb}(\text{NEt}_2)_4$	587s	1000vs	1153s	1185vs
$\text{EtN}=\text{Ta}(\text{NEt}_2)_3$	585m	1005vs	1152m	1188s
$\text{Th}(\text{NEt}_2)_4$	540s	998s	1160s	1183s

* All spectra in cyclohexane solution.

characteristic ligand bands for some metal diethylamides. The tetrakis-derivatives show one metal-nitrogen band as expected for a tetrahedral MN_4 system and as with the dimethylamides the M-N frequencies for first-row metals are significantly higher than for second- and

third-row metals. The monomeric monoethylimidotris-diethylamidotantalum $\text{EtN}=\text{Ta}(\text{NEt}_2)_3$ showed only one metal-nitrogen band whereas for local C_{3v} symmetry three metal-nitrogen stretches would be expected corresponding to $\text{M}=\text{N}$ stretching (A_1) and $\text{M}-\text{N}$ stretching (A_1 , E). The observed band (585 cm^{-1}) is obviously due to the $\text{M}-\text{N}$ stretching mode (E) and there is a very weak band at 495 cm^{-1} which might be the A_1 mode. The $\text{M}=\text{N}$ band (A_1) may well be in the 1000–1200 cm^{-1} region where it would be obscured by one of the strong ligand bands.

Metal-Nitrogen Stretching Frequencies.—The metal-nitrogen stretching frequencies for a number of metal alkylamides are given in Table 3. For the tetrakis-

TABLE 3

Metal-nitrogen stretching frequencies (cm^{-1})

Ligand L	TiL_4	ZrL_4	HfL_4	$\text{RN}=\text{TaL}_3$
Me_2N	592	537	533	—
Et_2N	610	577	577	585 ^a
Pr^n_2N	667	637	637	630 ^b
Bu^n_2N	667	637		634 ^c
Bu^n_2N	700	677		
MeBuN	640	606	605	608 ^e
$\text{C}_5\text{H}_9\text{N}^d$	640	620	620	625 ^e
$\text{CH}_3\text{C}_5\text{H}_9\text{N}^f$...	667	601	600	

Spectra are in cyclohexane solution.
 $\text{R}^a = \text{Et}$; $\text{R}^b = \text{Pr}^n$; $\text{R}^c = \text{Bu}^n$; $\text{R}^d = \text{piperidide}$; $\text{R}^e = \text{TaL}_3$; $\text{R}^f = 2\text{-methyl piperidide}$.

dialkylamido-compounds of Ti, Zr, and Hf the order of frequencies is: $\text{Bu}^n_2\text{N} > \text{Bu}^n_2\text{N} \sim \text{Pr}^n_2\text{N} > \text{Et}_2\text{N} > \text{Me}_2\text{N}$, for each metal. Since an increase in mass of the ligand NR_2 should cause a decrease in M-N frequency the observed increasing order $\text{Me}_2\text{N} < \text{Et}_2\text{N} < \text{Pr}^n_2\text{N}$ cannot be due to the mass effect. Steric interactions will increase in the order $\text{Me}_2\text{N} < \text{Et}_2\text{N} < \text{Pr}^n_2\text{N} < \text{Bu}^n_2\text{N} < \text{Bu}^n_2\text{N}$ but by weakening the M-N bonds should also decrease the metal-nitrogen frequencies. Therefore the observed order must reflect an electronic factor unless coupling between metal-nitrogen and ligand vibrations is responsible. A simple explanation in electronic terms involves the postulate

of nitrogen $\rightarrow$ metal $p_\pi-d_\pi$ bonding $\bar{\text{M}}=\text{NR}_2$ which would be supported by the inductive ($+I$) effect of the alkyl groups. The piperidide ligand has a steric effect comparable with NMe_2 but its inductive effect should be roughly between NEt_2 and NPr_2 and it is noteworthy that the M-N frequencies of the piperidides are all between those of the diethylamides and di-n-propylamides. Similarly, with the frequencies for $\text{M}(\text{NMeBu}^n)_4$ compounds. Thus all of the data in Table 3 are consistent with an electronic explanation. It is well established that in transition-metal compounds the metal atom tends to achieve an 18-electron valency shell and in the $\text{M}(\text{NR}_2)_4$ molecules a share of 16-electrons could be obtained if all of the nitrogen lone-pairs were involved in $p_\pi-d_\pi$ bonding (*cf.* 16-electron group in Cp_2MX_2 compounds). With the tantalum compounds $\text{RN}=\text{Ta}(\text{NR}_2)_3$ the participation of all nitrogen lone-pairs in π -bonding would contribute to an 18-electron

valency shell (*cf.* Cp_2TaX_3) and would imply some triple bond character ($\text{RN}\equiv\text{Ta}$) in the alkylimidotantalum group.

Previous work² showed that compounds of the type $\text{Ti}(\text{NR}^1_2)_x(\text{NR}^2_2)_{(4-x)}$ could be synthesized by transamination reactions. In view of the considerable difference in Ti-N frequency between Ti-NMe_2 and Ti-NPr^n_2 the compounds $\text{Ti}(\text{NMe}_2)_x(\text{NPr}^n_2)_{(4-x)}$, ($x = 1-3$), were prepared and their i.r. spectra measured with the view to studying the effect of ligand substitution on metal-nitrogen stretching frequency. Since each compound is monomeric the number of i.r.-active Ti-N bands observed should depend on the symmetry behaviour of the TiN_4 pentatomic group although strong coupling between Ti-N and ligand vibrations may invalidate this approach. For localised T_d symmetry each compound should give a single band $\nu_3(F_2)$ with the frequency increasing from 592 cm^{-1} in $\text{Ti}(\text{NMe}_2)_4$ to 667 cm^{-1} in $\text{Ti}(\text{NPr}^n_2)_4$. However, if the $\text{Ti}\cdots\text{N}$ bond in the TiNMe_2 group is sufficiently different from that in the TiNPr^n_2 group, as suggested by the difference in frequencies of the tetrakis-compounds, then in the 'mixed' compounds $\text{Ti}(\text{NMe}_2)_x(\text{NPr}^n_2)_{(4-x)}$ the localised symmetry may be lower than T_d namely C_{3v} ($x = 1$ or 3) or C_{2v} ($x = 2$) and more Ti-N frequencies should appear. In fact each 'mixed' compound gave two Ti-N stretching frequencies one near to the Ti-NMe_2 frequency and the other near to the Ti-NPr^n_2 frequency. Thus $\text{Ti}(\text{NMe}_2)_3(\text{NPr}^n_2)$ gave a strong band at 592 cm^{-1} and a weaker one at 660 cm^{-1} . For C_{3v} symmetry three Ti-N vibrations are i.r.-active ($2A_1, E$) and therefore we assign the 592 cm^{-1} band to the E mode and the 660 cm^{-1} band to the A_1 mode, whilst the other A_1 mode is expected to be near in frequency to the $\nu_1(A_1)$ Raman-only band in $\text{Ti}(\text{NMe}_2)_4$ which Bürger *et al.*⁶ assigned to the Raman band at 532 cm^{-1} . No band appeared in the range 532–592 cm^{-1} and we conclude that either the second A_1 mode is too weak to be detected in solution or that its frequency is too close to that of the E mode for it to be resolved. In $\text{Ti}(\text{NMe}_2)(\text{NPr}^n_2)_3$ there was a strong band at 667 cm^{-1} (E) and a weaker band at 571 cm^{-1} (A_1). The second A_1 mode would be expected near 600 cm^{-1} but it may be accidentally degenerate with the 571 cm^{-1} band. A rather weak third band was observed at 525 cm^{-1} which might be the other A_1 mode. For C_{2v} symmetry in $\text{Ti}(\text{NMe}_2)_2(\text{NPr}^n_2)_2$ four Ti-N bands are required ($2A_1, B_1, B_2$) and three bands were observed at 660m, 590s, and 560w cm^{-1} . If we assign the bands at 590 (B_1) and 560 (A_1) to Ti-NMe_2 bonds and the 660 (B_2) band to Ti-NPr^n_2 bonds then there should be another Ti-NPr^n_2 band (A_1) at >660 cm^{-1} but none was detected between 660 and 740 cm^{-1} .

N.M.R. Spectra.—In cyclohexane solution the tetra-kisdimethylamido-compounds $\text{M}(\text{NMe}_2)_4$ ($\text{M} = \text{Ti, Zr, Hf}$) gave the expected single methyl-proton peak for a monomeric species. Our value for $\text{Ti}(\text{NMe}_2)_4$ (τ 6.960)

is close to that obtained by Moedritzer⁷ on the neat liquid (τ 6.967) whilst Bürger *et al.*⁶ reported τ 6.99 for a cyclohexane solution. Moedritzer also measured the chemical shifts of dimethylamido-compounds of nonmetals and metalloids and his data are compared in Table 4 with ours on the metal derivatives. There is

TABLE 4
Chemical shifts of dimethylamido-compounds

Compound	τ	Electronegativity of central atom ^c
$\text{P}(\text{NMe}_2)_3$	7.575 ^a	2.1
$\text{As}(\text{NMe}_2)_3$	7.467 ^a	2.0
$\text{Sb}(\text{NMe}_2)_3$	7.300 ^a	1.8
$\text{Si}(\text{NMe}_2)_4$	7.583 ^a	1.8
$\text{Ge}(\text{NMe}_2)_4$	7.437 ^a	1.8
$\text{Ti}(\text{NMe}_2)_4$	6.960 ^b	1.6
$\text{Zr}(\text{NMe}_2)_4$	7.098 ^b	1.5
$\text{Hf}(\text{NMe}_2)_4$	7.083 ^b	1.4

^a Measurements by Moedritzer⁷ on neat liquids. ^b Measurements in cyclohexane solution, present research. ^c From W. Gordy and W. J. O. Thomas, *J. Chem. Phys.*, 1956, **24**, 439.

no correlation between τ value and electronegativity and clearly other factors such as neighbour-anisotropy effects contribute to the chemical shift. The single peak observed for $\text{Zr}(\text{NMe}_2)_4$ showed that although polymeric species are present ($n = 1.22$),² in which presumably bridging dimethylamido-groups would have a different chemical shift from terminal groups, intra- and inter-molecular exchange must be rapid on the n.m.r. timescale. To check the validity of this conclusion we measured the n.m.r. spectrum of $\text{Zr}(\text{NMe}_2)_4$ in methylene chloride over the range +30 to -40°. With a decrease in temperature from +30 to -10° the signal broadened and shifted slightly upfield from -175.0 to -173.0 c./sec. (relative to tetramethylsilane). At -20° a new unresolved peak (-172.8 c./sec.) appeared in the low-field side of the main peak (-171.5 c./sec.). At lower temperatures the 'new' peak increased in intensity at the expense of the original main peak and at -30° they were approximately equal (-172.5 and -171.0 c./sec.) whilst at -40° the 'new' peak (-173.5 c./sec.) predominated over the higher field peak (-172.3 c./sec.). The sequence of spectra were reproducible in ascending or descending order of temperatures suggesting that the equilibrium between monomers and polymers is markedly temperature-dependent. On steric grounds it is unlikely that the zirconium could be more than penta-co-ordinated by dimethylamido-groups and the polymers so formed would have a 1:3 ratio of bridging: terminal groups. With the assumption that intermolecular exchange of ligands between monomer and polymer species is slower than intramolecular exchange of ligand between terminal and bridging positions in the polymer (probably a dimer or trimer) then in the partly resolved spectra (-20 to -40°) the low-field peak is due to the averaged terminal-bridging groups of the polymer and the higher-field peak is due to monomer.

N.m.r. spectra were determined for several other dialkylamido-derivatives and the results for the chemical shifts of the α -protons are shown in Table 5 together with

⁷ K. Moedritzer, *Inorg. Chem.*, 1964, **3**, 609.

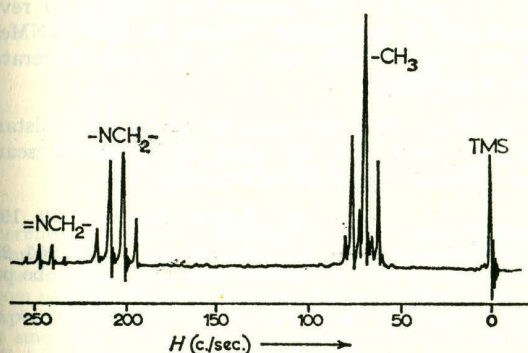
TABLE 5

Chemical shifts (α -protons) of metal dialkylamides

Ligand L	TiL ₄	ZrL ₄	HfL ₄	HL
NMe ₂	-182.4	-174.1	-175.0	-140.5
NEt ₂	-211.2	-196.5	-197.5	-156.0
NPr ⁿ ₂	-203.2	-189.8	-189.8	-152.0
NBu ⁿ ₂	-205.8	-191.5	-191.5	-156.0
NMeBu ⁿ	-183.0	-173.8	-173.7	-140.8
NMeBu ⁿ	-200.0	-187.8	-189.0	-150.8
Piperidide (NC ₅ H ₁₀)	-213.4	-201.0	-200.8	-162.5

Measurements in cyclohexane solution, in c./sec. relative to internal tetramethylsilane at 60 Mc./sec.

data for the parent amines. Generally the metal compounds have chemical shifts 30–50 c./sec. downfield from that of the parent amine. The diethylamides gave well-resolved quartet and triplet peaks for the α and β -protons although the lines were somewhat broad but the longer chain dialkylamides gave more complex

The n.m.r. spectrum of EtN=Ta(NEt₂)₃

partially resolved spectra which could be due to intramolecular congestion in M(NR₂)₄ which restricts rotation in the alkyl chains. Thus the spectrum of Prⁿ₂NH was simpler than for Ti(NPrⁿ)₄.

The n.m.r. spectra of the remarkable alkylimidotrisdialkylamidotantalum compounds RN=Ta(NR₂)₃ gave a striking confirmation of the presence of two different ligands in the correct proportions. In EtN=Ta(NEt₂)₃ (see Figure) the ethylimido methylene quartet was clearly resolved 38.5 c./sec. downfield from the methylene quartet of the diethylamido-groups. The two methyl triplets were also resolved but were too close (3.7 c./sec.) to be separated. In Table 6 the chemical

TABLE 6

Chemical shifts (α -protons) for alkylimidotrisdialkylamidotantalums

Compound	=NR group	NR ₂ group
EtN=Ta(NEt ₂) ₃	-242.5	-204.0
Pr ⁿ N=Ta(NPr ⁿ) ₃	-239.5	-200.7
Bu ⁿ N=Ta(NBu ⁿ) ₃	-237.5	-201.0

Measurements in benzene solution, in c./sec. relative to internal tetramethylsilane at 60 Mc/sec.

shifts for the α -protons in three of these compounds are shown and in each case the protons of the imido-group are shifted nearly 40 c./sec. downfield from those of the

dialkylamido-groups. It was noteworthy in the spectrum of PrⁿN=Ta(NPrⁿ)₃ that the α -protons in the *n*-propylimido-group gave a sharp triplet whilst those in the di-*n*-propylamido-group gave a broader more complex spectrum like that of Ti(NPrⁿ)₄.

EXPERIMENTAL

All reactions were carried out under an atmosphere of oxygen-free dry nitrogen or argon and all apparatus and solvents were specially dried. The titanium-,² zirconium-,² niobium-,³ and tantalum-dialkylamides⁴ were prepared and purified by the methods of Bradley and Thomas. Hafniumdialkylamides were prepared from the tetrachloride by similar methods. From HfCl₄ (16.0 g.) and LiNEt₂ (from 30 ml. Et₂NH and 118 ml. of 1.7*N*-*n*-butyllithium in *n*-hexane) was isolated yellow liquid Hf(NEt₂)₄ (12.5 g.; b.p. 130–135°/0.1 mm.; Found: Hf, 38.5. Required: Hf, 38.2%). From the reaction of Hf(NEt₂)₄ (12.5 g.) and piperidine (100 ml.) in cyclohexane (50 ml.) was isolated yellow Hf(NC₅H₁₀)₄ (10.0 g., b.p. 135–140°/0.1 mm. (Found: Hf, 35.0. Required: Hf, 34.7%). Similarly, V(NMe₂)₄ (green solid; sublimes 80°/0.1 mm., Found: V, 22.5. Required: V, 22.4%) and V(NEt₂)₄ (green liquid; b.p. 120–130°/0.1 mm.; Found: V, 14.8. Required: V, 15.0%) were prepared from vanadium tetrachloride and the appropriate lithium dialkylamide. Only very small yields of Th(NEt₂)₄ (yellow solid; b.p. 130–140°/0.1 mm.) could be obtained from the ThCl₄-LiNEt₂ reaction which was tried in various solvents (*e.g.* *n*-hexane, diethylamine, diethyl ether, tetrahydrofuran, and mixtures) and the product was characterised by qualitative analysis for thorium and diethylamide and by i.r. and n.m.r. spectroscopy. Special attention was given to the purification of the alkylimido-trisdialkylamidotantalum compounds which are contaminated with some Ta(NR₂)₄ as prepared by the method of Bradley and Thomas.⁴ Fractional distillation under reduced pressure with a spinning-band column served to isolate the slightly more volatile RN=Ta(NR₂)₃. The valency analysis^{3,4} was used in conjunction with tantalum analysis to check the identity of the products. The results are given in Table 7.

TABLE 7

Analytical data and volatility of RN=Ta(NR₂)₃ compounds

Compound	Ta (%)		Valency Found	Volatility (°c/mm.)	Colour
	Found	Calc.			
EtN=Ta(NEt ₂) ₃	40.2	40.7	4.93	95— 105/0.1	Yellow
Pr ⁿ N=Ta(NPr ⁿ) ₃ ...	33.5	33.6	4.96	120— 125/0.2 *	Yellow
Bu ⁿ N=Ta(NMeBu ⁿ) ₃	35.4	35.0	4.97	150— 155/0.1 *	Orange
Bu ⁿ N=Ta(NBu ⁿ) ₃ ...	28.2	28.4	4.94	180— 195/0.1 *	Orange

* Bath temperatures not true boiling points.

I.r. Spectra.—The i.r. spectra were obtained with a Beckman IR-7 (4000–650 cm.⁻¹) and IR-5A (CsBr optics) (900–300 cm.⁻¹) double-beam instruments. Frequency checks were made periodically with polystyrene and 1,2,4-trichlorobenzene. Solutions were prepared and introduced into KBr cells in a dry-box. Since the metal-dialkylamides reacted vigorously with carbon disulphide to

form *NN*-dialkyldithiocarbamates⁸ and more slowly with carbon tetrachloride and methylene dichloride it was necessary to use hydrocarbon solvents for the i.r. spectra. The results recorded here were all determined in 0.1M-cyclohexane solutions but several concentrations were examined in each case with special attention to balancing-out solvent bands to ensure that the spectra obtained belonged to the metaldialkylamide. In addition to the characteristic bands listed in Tables 1–3, the compounds also had bands as follows:

Metal Dimethylamides.—2960–2800s, 2808–2760vs, 1429–1413m, and 1131–1117m cm⁻¹.

Methyl Diethylamides.—2990–2820 (2 s bands), 2675–2630 (2 m–w bands), 1475–1467w, 1370–1365s, 1355–1349s, 1340–1327m, 1280–1265m, 1064m, 1048–1040m, 880–867s, 793–787s, 506–480m cm⁻¹.

Metal Di-n-propylamides.—2980–2760vs, 2730–2630m, 1467–1454s, 1376s, 1364–1360s, 1300m, 1247–1245w, 1178m, 1147s, 1105m, 1087–1082m, 1032m, 973–966vs, 885m, 871–867m, 844w, 773w, 747–742w, and 503–500w cm⁻¹.

Metal Di-n-butylamides.—2972–2817s, 2735–2732w, 1467s, 1377s, 1364–1359s, 1343m,sh, 1310w, 1265m, 1236w, 1221m, 1169s, 1146s, 1116–1112m, 1088m, 1013s, 961m, 913s, 898s, 851–847m, 744w, 731w, 510–505w cm⁻¹.

Metal Di-isobutylamides.—2985–2825s, 2660–2640m, 1472–1450s, 1384s, 1366s, 1306s, 1145s, 1100–1093s, 1047–1037m, 983vs, 953s, 926–920s, 876s, 820–815m, 795–767m, 743w.

Metal Di-methyl-n-butylamides.—2975–2885s, 2808–2800s, 2775s, 1467s, 1415–1408m, 1377m, 1359s, 1311m, 1270–1266m, 1243m, 1193s, 1149s, 1117–1111m, 1083s,

1001s, 981s, 950–946s, 924–919vs, 898m, 857–847m, 747–740w cm⁻¹.

Metal Piperidides.—2800vs, 2786vs, 1439m, 1359–1356vs, 1340m, 1307s, 1270m, 1252m, 1195s, 1146s, 1105s, 1054s, 1020vs, 954w, 916–907vs, 901s, 850s, 821s, 750–740m, 515–496m cm⁻¹.

Metal 2-Methylpiperidides (data in italics for *Ti*-derivative only).—2970s, 2808s, 1524w, 1450s, 1361s, 1339s, 1327m, 1302w, 1276m, 1221m, 1199s, 1176m, 1142s, 1126s, 1117m,sh, 1102m, 1065s, 1054s, 996m,sh, 980s, 894s, 890–880s, 874vs, 847m, 825–816m, 800m, 786m, 545–535s, 448m cm⁻¹.

N.m.r. Spectra.—Measurements were made on a Varian A-60 instrument.

The results given in Table 5 were obtained in cyclohexane solution (40%; w/v) at 37° with internal tetramethylsilane calibrant. Experiments at various concentrations from neat liquid down to 10–15% solutions in cyclohexane showed no systematic change in chemical shift with a maximum change of 0.5 c./sec. The compounds in Table 6 were measured in benzene to reveal the positions of the methyl triplets in EtNTa(NMe₂)₃. Methylene chloride was used for the low-temperature studies on Zr(NMe₂)₄.

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Rates of Water-catalysed Reactions in Water-Deuterium Oxide Mixtures

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La Mer and Greenspan's measurements (*Trans. Faraday Soc.*, 1937, **33**, 1266) on the rate of the water-catalysed decomposition of nitramide and new results on the hydrolysis of acetic anhydride in H₂O–D₂O mixtures are analysed in terms of the theory of H₂O–D₂O systems. The results are shown to bear a qualitative resemblance to the thermodynamic isotope effect on the ionic product of water in H₂O–D₂O mixtures. They can be quantitatively accounted for in terms of transition-state models, consistent with the conclusions of other mechanistic studies, in which there is an *incipient* charge separation similar to the complete charge-separation in ionised water.

WHILST the interpretation of changes in the composition of H₂O–D₂O solvents on the rates of acid-catalysed reactions has received a good deal of attention in recent years, there seems to have been little interest in the theory of the corresponding solvent effects on rates of so-called 'spontaneous' or 'water-catalysed' reactions.¹ The present paper applies the theory of H₂O–D₂O solvent isotope effects to kinetic results for two representative reactions of this class. The rate data are old results for the decomposition of nitramide,² and new measure-

ments of the hydrolysis of acetic anhydride. For both reactions the character of the curves relating rate constant to isotopic solvent composition (expressed by *n*, the atom fraction of deuterium) differs from that for typical acid-catalysed reactions. The water-catalysed reactions proceed more slowly in D₂O than in H₂O but, in contrast to those acid-catalysed reactions to which the same statement applies, the curves are *convex* towards the composition axis (Figure 1). However, this shape is similar to that found for the variation of the ionic product of water (*K_w*) with solvent composition,^{3–5}

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