

TABLE 2—PARAMETERS OF EQ. 1 FOR THE REACTION BETWEEN COPPER (PLATE) AND IODINE (SOLID AND VAPOUR) AT DIFFERENT TEMPERATURES

Temp. (°K)	$K \times 10^5$ (g ² /hr)	$C \times 10^5$ (g ²)
COPPER-IODINE (SOLID) SYSTEM		
303	2.99	2.00
313	5.67	6.05
323	9.33	14.00
333	11.57	25.50
343	14.61	36.00
COPPER-IODINE (VAPOUR) SYSTEM		
303	3.00	—
313	11.63	—
323	21.62	—
333	39.58	—
343	71.87	—

tical density of the product films and the dimensions of the metal plate, are 0.0030 cm and 0.0043 cm respectively. In this thickness range of coherent product films, the parabolic equation is obeyed^{1,2}. Another condition for the applicability of the parabolic equation is low conductivity of reaction product, which is satisfied in this case⁷. The reactions between copper and iodine (solid) and copper and iodine (vapour) are diffusion-controlled, where the diffusion of reacting species determines the rate of the reaction. The film is coherent and protective and controls the diffusion in the course of reaction. The agreement between the present experimental and the earlier reported values⁶ (12.4 kcal/mole) of the energy of activation suggests that the reaction mechanism at high as well as the ordinary temperature is the same.

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Reactions of Anhydrous Inorganic Nitrates in Dimethylformamide-Acid Chloride Adducts

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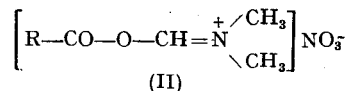
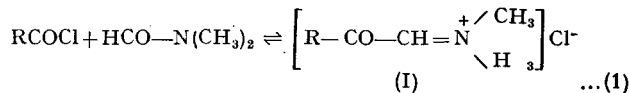
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Inorganic nitrates exchange anion with dimethylformamide-acid chloride adducts forming new adducts. These intermediates are very unstable and decompose

in an exothermic reaction evolving N₂O₄ and oxygen. These reactions may serve as an *in situ* source of oxygen in a nonaqueous medium.

ACID halide adducts of dimethylformamide (DMF) and their reactions have been reported earlier^{1,2}. The adducts generally exist in equilibrium with free DMF and acid halides (Eq. 1). Adducts (I) are very reactive due to the presence of $\text{C}=\overset{\oplus}{\text{N}}$ bond which is highly susceptible to nucleophilic reagents².



In order to understand the nature of anion in the adduct (I), an investigation has now been carried out to exchange the anion with more complex oxyacid anion such as nitrate. The exchange occurred spontaneously when sodium, potassium or calcium nitrates are used. But ammonium and silver nitrates reacted instantaneously accompanied by the decomposition of the new adduct (II). However, decomposition may be avoided by keeping the temperature at 0°. The exchange is always followed by precipitation of metal chloride.

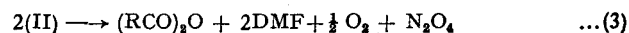
The reactivity of the salt seems to depend on the cationic part. The novel aspect of the exchange reaction is the subsequent decomposition pattern of the adduct (II). The adduct (II) decomposes spontaneously. The structure for II is attributed on the basis of adduct (I) whose structure is known^{1,2}. Similar structures have been assigned to DMF-Lewis acid adducts^{3,4}.

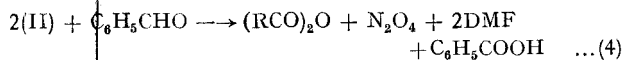
Adduct (II) differs from the other adducts of DMF so far known in that it possesses a more complex oxyacid anion. The instability of the adduct (II) may be attributed to the degree of freedom of oxyacid anion itself. Most aprotic dipolar solvents like DMF strongly interact with ionic Lewis acid type of compounds. Usually it is cationic part that is more firmly held by the dipolar molecule. The positive end of dipole is less accessible and hence the anion of the Lewis acid is relatively free to be very reactive⁵. For this reason the reactivity of the anionic part of II is responsible for the instability of the adduct as a whole. The existence of the anion in a non-aqueous medium may have partially contributed to the instability of the adduct.

Ingold^{6,7} observed that the nitrating power of any acyl nitrate is due to the existence of an equilibrium (Eq. 2) and that it is the N₂O₅ that

$$2\text{R}-\text{CO}-\text{O}-\text{NO}_2 \rightleftharpoons (\text{R}-\text{CO})_2\text{O} + \text{N}_2\text{O}_5 \quad \dots(2)$$

nitrates rather than acyl nitrate itself. Normally, for nitration, NO₂⁺ is necessary which is not generated in the decomposition of adduct (II). This accounts for the failure of II to nitrate anisol, while acyl nitrate accomplishes the reaction with ease. The course of decomposition of II is given in Eq. (3).





The evidence for the evolution of oxygen from II is clearly indicated by its capacity to oxidize benzaldehyde stoichiometrically (Eq. 4). Even though a definite mechanism for the decomposition of II cannot be projected at this stage, this reaction serves as useful non-aqueous oxidation system. An important aspect of the decomposition is its irreversibility while there is an equilibrium for acyl nitrates. A control experiment, carried without adding the nitrate did not indicate any significant oxidation of benzaldehyde.

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Thermal Behaviour of Cu(II), Ni(II) & Pd(II) Chelates of 2-Hydroxy-1-naphthaldoxime

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Thermal studies of 2-hydroxy-1-naphthaldoxime and its copper(II), nickel(II) and palladium(II) chelates have been carried out. The order of thermal stability is found to be Pd > Ni > Cu. The results obtained are compared with the data available in the literature for structurally similar oximes. The advantages of the reagent for the thermogravimetric analysis of metal ions have been discussed.

THE reagent, 2-hydroxy-1-naphthaldoxime, has been employed for the gravimetric determination of many metal ions¹⁻³. The present communication deals with the thermal analysis of 2-hydroxy-1-naphthaldoxime chelates of copper(II), nickel(II) and palladium(II) for any possible correlation of the thermal stability with the structure.

A Stanton thermobalance, model HT-SM (range ambient 1600°) with an accuracy of 1 mg was used for recording TGA curves at a heating rate of 6°/min. The weights of the samples taken were as follows: 2-hydroxy-1-naphthaldoxime (81.0 mg); copper chelate (100.4 mg); nickel chelate (100.1 mg); and palladium chelate (85.8 mg).

DTA curves were recorded using a Netzsch (West Germany) differential thermal analyser (range 1550°) which was operated at heating rate of 10°/min. The samples, approximately 100-200

mg in weight, were placed in the platinum crucible and the temperature measured with a Pt and Pt-Rh thermocouple. Kaoline was used as reference.

The metal chelates investigated were prepared partly according to gravimetric analytical procedures and partly by the method described in our earlier communication³. These chelates which have 1:2 stoichiometry (metal-ligand) analysed satisfactorily for metal contents⁴. All the chelates are powders, the colours being light brown, green and bright yellow for copper, nickel and palladium complexes respectively.

The oxime and the chelates are found to be thermally stable up to 200°. This indicates that the chelates are not hydrated. The initial decomposition temperatures interpolated from the TGA and DTA curves are taken as a measure of the thermal stability of the compounds. An examination of the DTA curves showed that exothermic reactions occurred in all the chelates, indicating that the chelates did not melt but decomposed. An inspection of the TGA curves of the metal complexes indicated a sharp initial decomposition associated with a rapid loss in weight in which the ligand is almost completely lost. In the case of palladium the increase in weight above 470° may probably be due to partial oxidation of the metal while at higher temperatures the metal is generated. The pyrolysis of copper and nickel chelates above 540° corresponds to the oxide stage (Table 1). This suggests that in the case of palladium chelate alone the thermal decomposition is preceded by the scission of the metal-ligand bond.

The TGA curves of copper, nickel and palladium complexes of 2-hydroxy-1-naphthaldoxime show that these chelates are much more stable than those of salicylaldoxime and nioxime^{5,6} and are nearly as stable as the chelates of resacetophenoneoxime⁹. 2-Hydroxy-1-naphthaldoxime therefore appears to be a better reagent than salicylaldoxime and nioxime for the automatic thermogravimetric determination of these metal ions. The recommended temperatures for the drying of nickel and palladium chelates of dimethylglyoxime⁶ in the gravimetric determination are 79-171° and 45-171° respectively. In the case of 2-hydroxy-1-naphthaldoxime complexes the drying can be affected at a much higher temperature. These facts coupled with the most favourable gravimetric factor makes 2-hydroxy-1-naphthaldoxime a better gravimetric reagent than dimethylglyoxime for copper, nickel and palladium.

TABLE 1 — DECOMPOSITION TEMPERATURES AND PYROLYSIS PRODUCTS OF LIGAND AND ITS CHELATES

Substance	Decomp. temp. (°C)		Residue percentages		
	TGA	DTA	Expl.	Theor.	
				Metal	Oxide
2-Hydroxy-1-naphthaldoxime	205	225	—	—	—
Copper chelate	225	245	17.7	14.6	18.2
Nickel chelate	275	290	16.9	13.6	17.3
Palladium chelate	285	290	22.6	22.2	25.6