



Fig. 2. Change in the relative radical concentration in X-irradiated methionine after exposure to ultra-violet

described^{1,2}, operates in the X-band and with a TE_{102} rectangular mode. The d.c. magnetic field is modulated at a frequency of 100 kc/s. To avoid saturation effects in the irradiated sample the microwave energy of the klystron was sufficiently attenuated. Synthetic ruby was used as a secondary standard³. The resonance occurs far from $g = 2$, permitting simultaneous observation of both standard and sample. The ruby was calibrated by comparison with a 5×10^{-5} mol solution of diphenyl picryl-hydraxyl (DPPH) in oxygenated carbon tetrachloride. The number of electron spin resonance centres in the irradiated sample was obtained by integration^{4,5}.

After irradiation of the methionine a very characteristic pattern of the electron spin resonance spectrum was obtained (Fig. 1, solid line), which does not show the typical cysteine-cystine spectrum of the so-called sulphur localized radical⁶, and no change was observed in keeping the samples at room temperature. Before the ultra-violet irradiation the radical concentration of the X-irradiated methionine was 1.5×10^{17} spins/g. It must be mentioned that the error of the absolute measurements of the radical concentration is at least 50 per cent⁷. For technical reasons, the X-irradiated samples could only be measured some hours after irradiation and the samples were stored at -17°C . Irradiation of the X-irradiated methionine with ultra-violet leads to rapid decay of the radical concentration, which reaches a minimum after 30 min and then increases again (Fig. 2). The increase of the radical concentration is produced by a new radical. The new signal lies in the region of lower magnetic field strength (Fig. 1, dotted line). Besides the formation of the ultra-violet-induced signal the formation of sulphuretted hydrogen was detected and the sample turned brown. The ultra-violet rays of longer wave-lengths ($\lambda > 285 \text{ m}\mu$) quenched the X-ray signals of methionine without forming new signals which could be detected in our spectrometer. Whether the quenching of the X-ray-induced electron spin resonance centres is produced by photolytically produced sulphuretted hydrogen, by other radical fragments or by some semiconduction processes is now being investigated.

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N—C=O Bending Vibration in Complexes of Dimethylformamide with Metal Halides

SHIFTS to lower frequencies of the C=O stretching vibration on complex formation between metals and ligands containing the carbonyl group have been the subject of several investigations, following the work of Bellamy and Branch¹. A similar examination of the C=O bending vibration, to the best of our knowledge, has not been previously reported: so we investigated this vibration in complexes of amides.

An electron diffraction study of dimethylformamide² has indicated a planar CNCO skeleton with the carbon atom *cis* to the carbonyl group only slightly out of the plane. The N—CO bond distance is 1.34 Å, indicating, as expected, appreciable double bond character. A normal co-ordinate analysis has not been reported for this compound.

We have found only one absorption band in the 840–440 cm^{-1} region of the spectrum of liquid dimethylformamide. This absorption, at 657 cm^{-1} , is about as strong as that associated with the CH stretching vibrations and can be attributed essentially to the N—C=O bending vibration. Corresponding absorptions by other amides have been designated the amide IV band; in the spectrum of *N*-methylformamide this band is at 771 cm^{-1} (ref. 3).

This absorption has been observed to shift to higher frequencies in complexes of dimethylformamide with metal halides. The frequencies of the absorption maxima are listed in Table 1. Some of the complexes react with potassium halides; maxima for these compounds are listed in Nujol mulls. The shift in the N—C=O bending frequency is expected to increase with increasing strength of the CO—M bond. The data of Table 1 reveal that the shifts are in the order $\text{Zn} > \text{Mn} > \text{Cd} > \text{Pb}$. Two peaks were observed in the spectra of the iron, nickel and cobalt complexes; taking the mean of these two maxima, the shifts are in the order $\text{Fe} > \text{Zn} = \text{Ni} > \text{Co} > \text{Mn}$. With the possible exceptions of nickel and cobalt, these shifts appear to be related to the O—M bond strengths.

Table 1. ABSORPTION MAXIMA (CM^{-1}) IN NUJOL MULLS (N) AND POTASSIUM BROMIDE DISKS

Compound	Maxima	Compound	Maxima
DMF	657		
$\text{FeCl}_2 \cdot 2\text{DMF}$	697 681	$\text{CoI}_2 \cdot 2\text{DMF}$	689 678
$\text{ZnCl}_2 \cdot 2\text{DMF}$	688	$\text{MnCl}_2 \cdot 2\text{DMF}$	676
$\text{ZnBr}_2 \cdot 2\text{DMF}$	688	$\text{MnBr}_2 \cdot 2\text{DMF}$	678
$\text{ZnI}_2 \cdot 2\text{DMF}$	688	$\text{MnI}_2 \cdot 4\text{DMF}$	674
$\text{NiBr}_2 \cdot 2\text{DMF} \cdot 3\text{H}_2\text{O}$	696 684	$\text{CdCl}_2 \cdot 2\text{DMF}$	471 (N)
$\text{NiI}_2 \cdot 2\text{DMF}$	693 682	$\text{CdBr}_2 \cdot 2\text{DMF}$	677
$\text{CoCl}_2 \cdot 2\text{DMF}$	687 679	$\text{CdI}_2 \cdot 2\text{DMF}$	677 (N)
$\text{CoBr}_2 \cdot 2\text{DMF}$	689 678	$\text{PbBr}_2 \cdot \text{DMF}$	607 (N)

Spectra of other amides are more complicated in this region. A normal co-ordinate analysis of *N*-methylacetamide has indicated⁴ a C=O out-of-plane bending vibration at 600 cm^{-1} and a combination N—C=O bending and $\text{H}_3\text{C}-\text{C}$ stretching frequency of 627 cm^{-1} . We have observed maxima (cm^{-1}) at 473, 589 and 733 (ν) in the spectrum of liquid dimethylacetamide; values of 478, 596 and 742 for $\text{PbBr}_2 \cdot \text{DMA}$; 481, 598 and 744 for $\text{CdBr}_2 \cdot \text{DMA}$; and 484, 623 (and 601 (ν)) and 746 for $\text{ZnBr}_2 \cdot 2\text{DMA}$. The shifts are in the order $\text{Zn} > \text{Cd} > \text{Pb}$. The 733 cm^{-1} peak in the spectrum of the amide is greatly enhanced in the spectra of the complexes. The spectra of complexes of other amides are being investigated.

This work was supported by the U.S. Atomic Energy Commission.

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