

Absorption Spectrum of the OBr Radical

USING the flash photolysis technique of Norrish and Porter^{1,2} I have discovered a spectrum consisting of a series of roughly equidistant diffuse absorption bands which is attributed to the OBr radical. This spectrum was observed when mixtures of the vapours of bromo-substituted methanes and oxygen were irradiated by a flash discharge. Chloro-bromo-methane provided the most intense absorption bands, but they also appeared with the following compounds: CCl₃Br, CCl₂HBr, CBr₂H₂, CBr₄; the strongest bands were also weakly visible in mixtures of oxygen and ethyl bromide.

The intensity of the absorption decayed with a half-life of $\frac{1}{2}$ –1 msec., which falls into the range observed for radicals and metastable states. About fifteen diffuse absorption bands have been observed; the maxima, accurate to about 1 Å., are given in Table 1.

Table 1

Wave-length (Å.)	Frequency	Intensity	$\delta\nu$
3547	28,190 cm. ⁻¹	weak	
3484	28,700 cm. ⁻¹	weak	510 cm. ⁻¹
3435	29,110 cm. ⁻¹	weak	410 cm. ⁻¹
3383	29,560 cm. ⁻¹	strong*	450 cm. ⁻¹
3336	29,975 cm. ⁻¹	medium	415 cm. ⁻¹
3291	30,385 cm. ⁻¹	medium	410 cm. ⁻¹
3250	30,770 cm. ⁻¹	medium	385 cm. ⁻¹
3209	31,160 cm. ⁻¹	medium*	390 cm. ⁻¹
3170	31,545 cm. ⁻¹	strong*	385 cm. ⁻¹
3138	31,870 cm. ⁻¹	medium	325 cm. ⁻¹
3105	32,205 cm. ⁻¹	weak	335 cm. ⁻¹
3070	32,575 cm. ⁻¹	weak	370 cm. ⁻¹
3041	32,885 cm. ⁻¹	weak	310 cm. ⁻¹
3015	33,165 cm. ⁻¹	weak	280 cm. ⁻¹
2990	33,445 cm. ⁻¹	weak	280 cm. ⁻¹

* Fairly sharp limit on the short wave-length side.

It is surprising that this band system has never been observed during explosions sensitized by the flash-photolysis of bromine. In an investigation on the emission spectrum of flames to which bromine or methyl bromide had been added, Coleman and Gaydon³ observed some unidentified faint bands. They mention that the strongest heads appear to be at 3333 and 3384 Å. These wave-lengths coincide with two of the strongest bands given in Table 1.

The presence of oxygen, either as a mixture component or as an impurity in the added gas, is a prerequisite for the occurrence of the spectrum. The participation of bromine in the absorbing radical may be inferred from the fact that all the compounds from which the spectrum can arise must contain bromine. An absorber, consisting of more than two atoms, will probably result in a more complex spectrum, and it is difficult to see which common substance, other than BrO·, can result from the various mixtures of substituted bromomethanes and oxygen. Consequently, the radical OBr has been identified as the absorbing species although it is realized that no definite proof has been given.

The assignment of the spectrum to OBr also gives an explanation for the diffuseness of the bands, since it may be expected that the O—Br bond is very weak and thus easily dissociated. Predissociation from the high energy-level of the upper state is very probable. The fact that no absorption spectrum was observed when bromine was flashed in the presence of oxygen (in contrast to the corresponding case of Cl₂—O₂) can also be due to the weakness of the O—Br bond, which makes the reaction:



energetically impossible. This is also an indication that BrO₂, which is unstable at room temperature, is not the absorbing species. On the other hand, oxygen atoms will not react with bromine atoms in the formation of OBr radicals, since they cannot lose their energy. Indeed, no OBr bands were observed in an experiment in which a mixture of bromine and nitrogen dioxide was flash-irradiated.

It is believed that the formation of the OBr radical is possible in the present experiments as a result of the following occurrence. The flash dissociates the bromo-compound (RBr) into a bromine atom and a radical (R·). This will occur only if the bromo-compound has a sufficiently strong absorption. The introduction of more halogen atoms into the molecule increases the extinction coefficient, but decreases the vapour pressure. The maximum concentration of OBr will be greatest for that compound for which the product of extinction coefficient and vapour pressure is optimal. This is the case with CBrClH₂ and CBr₂H₂. The radical R· formed reacts with oxygen in the formation of ROO· in which the O—O bond is weakened to a large extent. On a subsequent collision with a bromine atom the OBr radical is formed.

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¹ Norrish and Porter, *Nature*, **164**, 658 (1949).

² Porter, *Proc. Roy. Soc., A*, **200**, 284 (1950).

³ Coleman and Gaydon, *Disc. Farad. Soc.*, **2**, 166 (1947).

Effects of Nuclear Irradiation upon the Decomposition of Lead Styphnate Monohydrate

THE thermal decomposition of lead styphnate monohydrate has been re-investigated prior to a study of the effects of gamma-ray and reactor irradiation upon the decomposition. The two previous studies^{1,2} of this decomposition gave quite divergent results.

A decomposition apparatus similar to those employed by other workers³ was used. Lead styphnate monohydrate was found to decompose reproducibly in the range found by the other investigators, that is, 197–228° C. Because of this small range of temperature available it was controlled to 0.1° C.

The decomposition curves of the present study fell into group C described by Garner and Haycock⁴; this group of decompositions is characterized by an initial small, fast gas evolution. This is followed by a linear period which develops into the acceleratory period. The initial gas evolution in lead styphnate monohydrate corresponded to about 1 per cent of the total gas evolved; this phase was followed by a linear region which developed into a parabolic acceleratory period. The inflexion point corresponded to 29 per cent reaction and was followed by a first-order deceleratory period. Rate constants for the acceleratory period were calculated from

$$(P - P_0) = k(t - t_0)^2$$