

Photographic Desensitisers and Oxygen

IN the course of experiments on the tracks on photographic plates due to protons set in motion by neutrons, we have made some observations of more general interest. We found that the rows of silver grains marking the tracks of swift particles only appeared after development when the plate had been treated with pinacryptol-yellow or some similar substance and when the exposure to the particles was carried out in air at reduced pressure or in nitrogen. We therefore investigated the effect of light on photographic emulsions similarly treated and exposed in air at different pressures or in different gases. Our results may be summarised thus:

- (1) The desensitisation is much reduced by (a) reduction of the air pressure; (b) by substituting pure nitrogen for air.
- (2) This effect is not so marked when the plate is moist.
- (3) The effect is apparent with pinacryptol-yellow, densitol, indulin-scarlet, phenosafranin, a mixture of pinacryptol-yellow and indulin-scarlet, antilumin and pinacryptol, but not with pinaflavol.
- (4) A reduced pressure has no influence on plates not desensitised by one of the substances before mentioned.

That this effect has not been noticed by Mr. Shivonen¹ in silver bromide sols is probably due to essential differences in the experimental conditions.

From our experiments we feel entitled to draw the conclusion that the dye itself only plays an auxiliary part, probably that of a catalyser, in the desensitisation process, the major part being played by the oxygen of the air. These results, therefore, appear to us to support the well-known oxidation theory of desensitisation due to Lüppo-Cramer.

The details of our investigation will be published in the *Sitzungsberichte der Akademie der Wissenschaften*.

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¹ *Z. wiss. Phot.*, 24; 1926.

Energy of the C-OH Bond and Molecular Structure in Alcohols

A CONTINUOUS absorption spectrum in the ultra-violet region which corresponds to the immediate dissociation of the molecule into its constituents was investigated for a number of alcohols in the vapour state. The radical OH is generally considered as pseudohalogen, and the dissociation products are considered to be the excited OH radical and the normal alkyl residue, analogous to a halogen-alkyl. So the dissociation energy in the accompanying Tables I and II, estimated from the absorption edge, must be modified, if the energy necessary to excite the OH radical is known. The data are not so accurate as the absolute values, but they seem to have a definite physical meaning as relative values and to be of sufficient interest to warrant publication.

A comparison of the results obtained with the

series of alcohols reveals certain interesting features on the relationship between the dissociation energy of the bond and the structure of the molecule.

TABLE I

Alcohols	Diss. Energy (kcal./mol.)	Raman Lines $\Delta\nu$ (cm. ⁻¹)
CH ₃ OH	133.6	1225
C ₂ H ₅ OH	137.5	1272
<i>n</i> -C ₃ H ₇ OH	140.9	1282
<i>n</i> -C ₄ H ₉ OH	141.9	1286
<i>n</i> -C ₅ H ₁₁ OH	142.3	
<i>n</i> -C ₆ H ₁₃ OH	142.7	
<i>n</i> -C ₇ H ₁₅ OH	143.4	
<i>n</i> -C ₈ H ₁₇ OH	144.5	
<i>n</i> -C ₁₀ H ₂₁ OH	150.2	
<i>n</i> -C ₁₁ H ₂₃ OH	152.2	

TABLE II

Alcohols	Diss. Energy (kcal./mol.)	Raman Lines $\Delta\nu$ (cm. ⁻¹)
<i>n</i> -C ₂ H ₅ OH	141.9	1286
<i>iso</i> -C ₂ H ₅ OH	141.2	1264
<i>sec</i> -C ₂ H ₅ OH	140.2	—
<i>tert</i> -C ₂ H ₅ OH	141.2	1202

(1) The energy of the C-OH bond increases successively as we go up the series of normal alcohols.

(2) In the isomers, no regularity appears among the energies of the C-OH bonds. It seems to assume the maximum value for the corresponding normal alcohols.

In connexion with the study of absorption in the ultra-violet region, it may be also worth while to compare the preceding results with the investigations of the Raman spectra of the corresponding alcohols. According to S. Venkateswaran and S. Bhagavantam¹, precisely the same relationships hold good in the series of alcohols as shown in Tables I and II.

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¹ S. Venkateswaran and S. Bhagavantam, *Ind. J. Phys.*, 5, 129; 1930.

A New Band System in Nitrogen

I HAVE recently directed attention in a letter which has been sent to the *Physical Review* for publication to some new nitrogen bands. Three of these bands degrading to the violet and having wavelengths 2536, 2635 and 2740 Å., have been found to increase in intensity as the pressure is lowered. This is true also of the new Appleyard-van der Ziel bands recently discussed by van der Ziel, and of the new system that is reported by me in the above-mentioned letter. The three bands have been identified as (0, 1), (0, 2) and (0, 3) bands of a new system, and their frequency differences agree well with those of the lower electronic state of the Appleyard-van der Ziel bands.

Further work is in progress in an attempt to obtain bands arising on higher vibrational states. Photographs taken at lower pressure may bring out such bands.

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