46. *Unstable Intermediates. Part I. Photochemical Reactions in Rigid Glasses.*

By M. C. R. SYMONS and M. G. TOWNSEND.

Highly reactive intermediates, formed by photolysis with ultraviolet light (2537 or 3650 Å), of dilute solid solutions of photosensitive compounds are often stabilised by being trapped in the glass. These intermediates, which are often free radicals, have been studied by spectrometric and electron-spin resonance methods: they are quite stable provided the glass is rigid, but are rapidly decomposed otherwise. The solvents included a variety of alcohols, carboxylic acids, saturated hydrocarbons, and vinyl compounds. The solutes included hydrogen peroxide, benzoyl peroxide, di-*tert.*-butyl peroxide, αα'-azo*iso*butyronitrile, and ethyl iodide. The nature of the trapped intermediates is discussed in terms of a generalised scheme for photolysis in rigid media.

WHEN reaction mechanism is considered it is often necessary to postulate the formation of intermediates which, because of their high reactivity, are never present in isolable or even in detectable quantities, and whose presence is therefore inferred because the proposed mechanism agrees with expectation or because the results of kinetic studies are adequately accommodated thereby. By suitable modification of the environment it is sometimes possible to build up concentrations of such intermediates sufficiently to permit of direct detection and study, particularly spectrometrically. We have studied how this may be accomplished; in particular, ultraviolet spectrophotometry and magnetic techniques are used to detect and study the intermediates.[1]

Lewis and Lipkin [2] described the changes in the electronic absorption spectra of organic molecules in dilute solution in rigid glasses at 70° K after ultraviolet irradiation. They obtained good evidence both for photodissociation into radicals and for photoionisation. Since then, spectrophotometry [3-5] and electron-spin resonance techniques [6] have also been used to study such photolysed glasses.[6] These two techniques being complementary, we aimed to combine them to examine the nature of the photochemical reactions in rigid media.

EXPERIMENTAL

Materials.—Hydrogen peroxide (90%, free from stabilisers) was kindly supplied by Laporte Chemicals Ltd. Water was distilled from alkaline permanganate, and other solvents were "AnalaR" or purified by standard procedures.

Glasses.—For electron-spin resonance studies, clear glasses were not essential, and provided a small fraction of the incident light penetrated some distance into the specimen, seemingly opaque solids could be used. For spectrophotometry studies it was necessary to obtain clear glasses, rigid at 100° K (the lowest temperature suitable for measurement with our apparatus), which did not shatter badly over a considerable time interval. These conditions were achieved for alcohols by adding small quantities of syrupy phosphoric acid, and for glycols and acids by adding up to 50% of water. *cyclo*Hexane (10%) was added to *cyclo*hexanol to prevent cracking. In cases for which no such additive was required, it was confirmed that their presence did not affect the characteristic changes in ultraviolet spectra.

Solute concentrations were varied in the range 10^{-1}—10^{-3}M.

Electron-spin Resonance Measurements.—These were made as described previously.[6] Spectra were recorded as the first derivative of the absorption band, the sample, contained in a thin

---

[1] Cf. Symons, *J.*, 1957, 387, 2186, 2440; Ingram and Symons, *J.*, 1957, 2437.

[2] Lewis and Lipkin, *J. Amer. Chem. Soc.*, 1942, **64**, 2801.

[3] Norman and Porter, *Proc. Roy. Soc.*, 1955, *A*, **230**, 399.

[4] (*a*) Sowden and Davidson, *J. Amer. Chem. Soc.*, 1956, **78**, 1291; (*b*) Linschitz, Berry, and Schweitzer, *ibid.*, 1954, **76**, 5833.

[5] Symons and Townsend, *J. Chem. Phys.*, 1957, **25**, 1299.

[6] Gibson, Ingram, Symons, and Townsend, *Trans. Faraday Soc.*, 1957, **53**, 914.

walled quartz tube, being placed directly in an H_{014} 3 cm. wavelength rectangular cavity cooled by liquid nitrogen.[6]

Spectrophotometric Measurements.—These were made by using a Unicam S.P. 500 spectrophotometer modified for use at low temperature. The irradiated glasses were contained in a cell constructed to avoid breakage caused by cracking of the glass consisting of two fused silica plates recessed into the bottom of a Perspex rod and enclosing an oval hole cut in the rod. The cell was filled by partly removing one plate, completely filling the cell, replacing the plate, and then immersion in liquid nitrogen. This procedure made it unnecessary to ensure that the cell did not leak slightly, and any reaction between the Perspex walls and the solution was reduced to a minimum.

The cell housing, described in detail elsewhere,[7] consisted of a box of black Perspex containing baffles through which a stream of cold gas could be passed. The cell, immersed in liquid nitrogen, contained in a Dewar flask attached to the bottom of the cell housing could be raised into the light path for measurement, and a heater, also immersed in the liquid nitrogen, could be regulated so that the rate of flow of cold nitrogen gas past the cell, and hence the temperature of the cell, could be controlled accurately.

The optical densities of the glasses, before and after irradiation, were measured against air. In order to obtain the spectra required, the experiments were repeated, under the same conditions, for pure solvent. These spectra were then subtracted after a suitable correction had been made for differences in the degree of cracking of the glasses by subtracting a zero reading, obtained by measurement in a region of the spectrum in which no specific absorption occurred, from optical densities at all wavelengths. (This correction depends upon the arbitrary assumption that scattering due to cracking is not a function of wavelength: thereby, the errors introduced are largely cancelled, since the corrections required were usually very similar.)

The lowest temperatures attained, measured by a thermocouple in the cell holder, were about 20° above the b. p. of the coolant. Whilst this was satisfactory for studying the most interesting spectra, it was not cold enough for studying spectra of species formed in certain solid hydrocarbon glasses such as those used by other workers.[3, 4a]

Photolyses.—Glasses in the cells immersed in liquid nitrogen, were irradiated with light, consisting largely of 2537 or 3650 Å wavelengths for periods of up to 6 hr. The sources were a low-pressure 150 w mercury arc with a discharge in the shape of a finger 4 in. long and jacketed by an evacuated quartz envelope (2537 Å), and a medium-pressure, 250 w mercury arc used in conjunction with an aluminised mirror. The low-pressure arc was immersed directly in the coolant, the evacuated envelope effectively preventing heat transfer which would otherwise extinguish the lamp.[6]

The small five-line electron-spin resonance signal detected after irradiation of ethanol glasses at 2537 Å is ascribed to ethanol radicals, $CH_3{\cdot}\dot{C}H{\cdot}OH$. These may arise from a variety of causes: (i) As the result of direct photolysis according to the equations:

$$CH_3{\cdot}CH_2{\cdot}OH \longrightarrow CH_3{\cdot}\dot{C}H{\cdot}OH + H{\cdot}$$

$$H{\cdot} + CH_3{\cdot}CH_2{\cdot}OH \longrightarrow H_2 + CH_3{\cdot}\dot{C}H{\cdot}OH$$

It is unlikely that 2537 Å light could accomplish this since there is no electronic absorption band in this region. However, low-pressure mercury lamps emit weakly in the 1900 Å region, where alcohols absorb strongly. Since ethanol exposed to ionising radiation gives a similar five-line spectrum [8, 9] it is possible that this is the process involved.

(ii) The radicals may arise by abstraction of hydrogen by photo-excited oxygen molecules fortuitously present in solution, or by hydrogen-atom exchange between ethanol and traces of acetaldehyde:

$$CH_3{\cdot}CH_2{\cdot}OH + CH_3{\cdot}CHO \longrightarrow 2CH_3{\cdot}\dot{C}H{\cdot}OH$$

Work now being undertaken may yield definite conclusions.

Similar electron-spin resonance spectra were sometimes recorded after exposure of alcoholic solutions to 2537 Å light. These signals were compared with those obtained from the solvent

---

[7] Symons and Townsend, *Spectrovision*, 1957, **4**, 5.

[8] Gordy and Luck, *J. Amer. Chem. Soc.*, 1956, **78**, 3240.

[9] Alger, Anderson, and Webb, *J. Chem. Phys.*, in the press.

alone under identical conditions, and if this proved to be appreciably less intense it was assumed that electron-spin resonance results gave no evidence for the formation of radicals from the substrate. This assumption, whilst open to question, will be made throughout the discussion. No electron-spin resonance signal was detected after irradiation of solvent with 3650 Å light, so this difficulty does not then arise.

RESULTS

Spectral details are summarised in the Table. Representative spectra are reproduced in Figs. 1, 2, and 3.

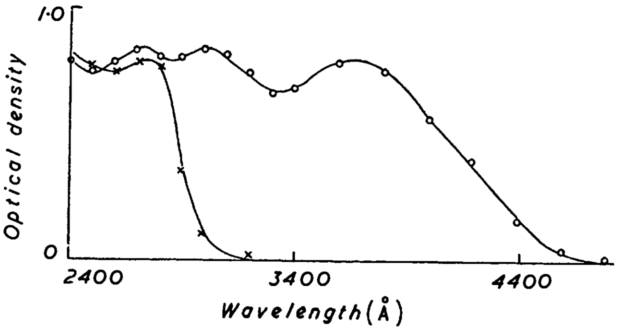


FIG. 1. *Spectrum of a solid solution of benzoyl peroxide in ethanol.*
–○– After irradiation with 2537 Å light.
–×– After warming to room temperature.

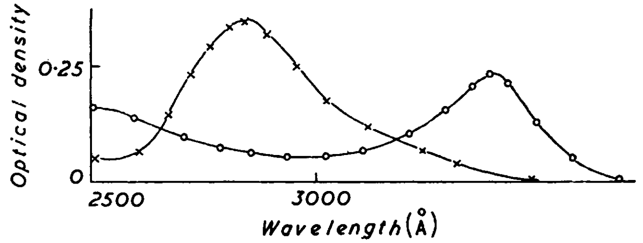


FIG. 2. *Spectrum of a solid solution of αα′-azoisobutyronitrile in ethanol.*
–○– Before irradiation.
–×– After irradiation with 3650 Å light.

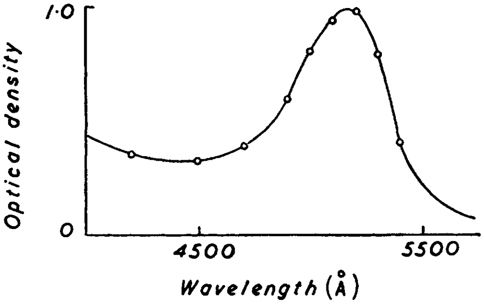


FIG. 3. *Spectrum of a solid solution of hydrogen peroxide in ethanol after irradiation with* 3650 Å *light.*

Photolysis of Hydrogen Peroxide.—In primary and secondary alcohols a violet colour appears after prolonged irradiation of dilute solutions. An extinction coefficient of about 300 was estimated for the band at 520 mμ by determination of the peroxide concentration before and after irradiation. This value is a lower limit because a radical-induced decomposition of residual hydrogen peroxide probably occurred during warming-up.

There is considerable speculation regarding the nature of the violet species. The following experiments were carried out in an attempt to clarify the situation (see p. 268). (*a*) The violet glasses were exposed to visible light for prolonged periods: no bleaching or change in the electron-spin resonance spectrum was detected. (*b*) Ethanol solutions were saturated with anhydrous lithium chloride: no change from the normal spectrum was detected after irradiation. (*c*) A solution of hydrogen peroxide in ethanol was degassed by repeated freezing under vacuum (10^{-4} mm.), and the container was sealed under vacuum before irradiation. Again, no change in the properties of the irradiated sample was apparent.

Striking evidence for the conversion of one unstable species into another before completion of reaction was obtained by studying the effect of a gradual increase in temperature upon the visible spectra of violet glasses containing excess of hydrogen peroxide. By slowly decreasing the rate of flow of cold gas through the cell-housing, it was possible to obtained a temperature gradient along the cell such that the lower portion remained violet, the centre became bright yellow, and the uppermost portion colourless. It proved very difficult to measure the spectra of the yellow glasses because it was impossible to prevent a cloudiness's appearing simultaneously with the yellow colour. However, in one attempt a marked shoulder in the 3700 Å region was recorded. It is suggested that the yellow compound is $HO_2{\cdot}$ formed by the reaction

$$R_2\dot{C}{\cdot}OH + H_2O_2 \longrightarrow R_2CH{\cdot}OH + HO_2{\cdot}$$

This reaction is energetically favourable compared with the alternative hydroxyl-radical displacement postulated by Merz and Waters.[10] The yellow colour is only observed when a large excess of peroxide is present. Livingston, Ghormley, and Zeldes [11] observed electron-spin resonance absorption in yellow solids obtained by condensing products from an electric discharge through water vapour. They consider that their results are best interpreted by the assumption that the paramagnetic species is $HO_2{\cdot}$.

Another example of colour change during softening of the glass is furnished by irradiated disulphur dichloride in methyl*cyclo*hexane. At 77° K this glass was intensely red, but on careful warming, the colour changed to blue before being lost entirely. Photolysis of a similar solution in 3-methylpentane, a softer glass, gave the blue species directly. Electron resonance studies showed that the glasses were paramagnetic, but the spectra are complex and insufficient is known to warrant discussion of the possible species formed. Sowden and Davidson also irradiated disulphur dichloride, but made no mention of colour.[3]

Photolysis of Ethyl Iodide.—No electron-spin resonance absorption attributable to radicals formed from ethyl iodide dissolved in ethanol was detected after irradiation for several hours. Willard and his co-workers [12] also failed to detect resonance from solid ethyl iodide after exposure to 2537 Å light, although a spectrum of six lines, attributed to ethyl radicals, was obtained after exposure to γ-radiation.

However, addition of iodine to the irradiated ethanolic solutions after warming-up resulted in the formation of tri-iodide, thus showing that iodide has been formed during photolysis. Willard and his co-workers [12] established conclusively that an important reaction during photolysis leads to the formation of ethylene and hydrogen iodide, $C_2H_5I \longrightarrow C_2H_4 + HI$, and our results suggest that this is the only important reaction occurring under our conditions.

*Photolysis of αα′-Azo*iso*butyronitrile.*—This nitrile, which is used extensively as a source of free radicals in vinyl polymerisation, has a band of low intensity at 340 mμ.[13] Photolysis with 3650 Å light caused a rapid shrinking of this band and a parallel increase in a band at 2850 Å. On warming to room temperature, this new band was also destroyed. No electron-spin resonance absorption was detected at any stage. The new band is very similar to that attributed by Talat-Erban and Bywater [13] to the unstable compound $Me_2C{:}C{:}N{\cdot}C(CN)Me_2$, for which they estimated a value of 125 for the extinction coefficient. We estimate a value of 25, assuming complete conversion of the αα′-azo*iso*butyronitrile into

---

[10] Merz and Waters, *J.*, 1949, S15.

[11] Livingston, Ghormley, and Zeldes, *J. Chem. Phys.*, 1956, **24**, 483.

[12] Luebbe and Willard, *J. Amer. Chem. Soc.*, in the press.

[13] Talat-Erban and Bywater, *J. Amer. Chem. Soc.*, 1955, **77**, 3712.

the species absorbing at 2850 Å, so if the new compound is $Me_2C{:}C{:}N{\cdot}C(CN)Me_2$ then the reaction

$$Me_2C(CN){\cdot}N{:}N{\cdot}C(CN)Me_2 \longrightarrow N_2 + Me_2C{:}C{:}N{\cdot}C(CN)Me_2$$

contributes about one-fifth to the total decomposition.

Other possible paths, not involving radicals, are

$$Me_2C(CN){\cdot}N{:}N{\cdot}C(CN)Me_2 \longrightarrow N_2 + Me_2C(CN){\cdot}C(CN)Me_2$$

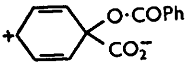
and

$$Me_2C(CN){\cdot}N{:}N{\cdot}C(CN)Me_2 \longrightarrow N_2 + Me_2CH{\cdot}CN + CH_2{:}C(CN)Me.$$

None of these products would be detected spectrophotometrically. When the nitrile was photolysed in a glass consisting largely of acrylonitrile, no polymer separated on warming. This is in contrast with the behaviour of a similar system in which the nitrile was replaced by hydrogen peroxide,[14] and the result provides further evidence for the absence of radicals.

Photolysis of Benzoyl Peroxide.—Benzoyl peroxide absorbs at 2750 Å, $\varepsilon_{max.} = 2340$. During the first few minutes of photolysis with 2537 Å light an intense yellow colour was observed. Two new bands were found at 3650 and 3050 Å and both were rapidly lost on softening. No electron-spin resonance absorption was detected. The extinction coefficient for the band at 3650 Å was found to be approximately 5600 by titrimetric estimation of the peroxide before and after irradiation. This is an upper limit if recombination can occur during warming-up.

It is possible that the unstable species is a non-radical such as the zwitterion (I), but it is also possible that the spectrum is due to benzoylperoxy-radicals which, for some reason, do not give rise to a detectable electron-spin resonance absorption. One way whereby this could occur would be for the radicals to be trapped so close together that the irradiated glass consists of isolated pairs of radicals, each sufficiently close to the other to give rise to spin–spin broadening. This could occur because of the large size and stability of benzoylperoxy-radicals. The magnetic interaction could spread out the resonance absorption beyond the limits of detection, but would not appreciably affect the ultraviolet absorption.



(I)

Absorption maxima ($\lambda_{max.}$ Å), *extinction coefficients* ($\varepsilon_{max.}$), *and electron-spin resonance results.* (*N* is the number of hyperfine lines.)

Solvent	Solute	Concn. (mol./l.)	Colour	$\lambda_{max.}$	$\varepsilon_{max.}$	*N*	
MeOH	H_2O_2	10^{-2}	Violet	5200	300	3	
EtOH	H_2O_2	10^{-2}	Violet	5200	300	5	
Pr^{n}OH	H_2O_2	10^{-2}	Violet	5200	300	5	
Pr^{i}OH	H_2O_2	10^{-2}	Violet	—	—	7	
*cyclo*Hexanol	H_2O_2	10^{-2}	Orange	4500	300	6	
tert.-Butanol	H_2O_2	10^{-2}	Colourless	—	—	3	
Diethyl ether	H_2O_2	10^{-2}	Violet	—	—	—	
Glycerol	H_2O_2	10^{-2}	Violet	—	—	1 [a]	
Ethylene glycol	H_2O_2	10^{-2}	Violet	—	—	1 [a]	
Acetic acid	H_2O_2	10^{-2}	Violet	—	—	*b*	
Formic acid	H_2O_2	10^{-2}	Violet	—	—	*b*	
Allyl alcohol	H_2O_2	10^{-2}	Yellow	—	—	4	
EtOH	$Me_3C{\cdot}O{\cdot}OH$	10^{-2}	Violet	—	—	5	
EtOH	$(Me_3CO)_2$	10^{-1}	Colourless	—	—	Nil [c]	*d*
EtOH	ClO_2	10^{-1}	Violet	—	—	*b*	
Methyl*cyclo*hexane	ClO_2	10^{-1}	Colourless	—	—	*b*	
EtOH	$(Ph{\cdot}CO_2)_2$	10^{-3}	Yellow	3650	6000	Nil [c]	*d*
Methyl*cyclo*hexane	$(Ph{\cdot}CO_2)_2$	10^{-3}	Yellow	—	—	Nil	*d*
EtOH	*e*	10^{-1}	Colourless	2850	—	Nil	
EtOH	EtI	10^{-1}	Colourless	—	—	Nil [c]	*d*
Methyl*cyclo*hexane	S_2Cl_2	10^{-1}	Red	—	—	*b*	*d*
3-Methylpentane	S_2Cl_2	10^{-1}	Blue	—	—	*b*	*d*

a = Signs of hyperfine structure. *b* = Complex spectrum. *c* = Small 5-line spectrum as found for EtOH alone. *d* = 2537 Å Radiation: otherwise 3650 Å. *e* = αα′-Azo*iso*butyronitrile.

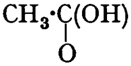
---

[14] Ingram, Symons, and Townsend, *Trans. Faraday Soc.*, 1958, **54**, 409.

DISCUSSION

In many instances the course of photolysis in rigid media seems to differ from that in fluid media or the gas phase. Sometimes a substance which is readily photolysed in solution is not decomposed at all when the medium is rigid.[4a] We have found, in agreement with Sowden and Davidson,[4a] that prolonged irradiation of a very dilute solution of iodine does not result in loss of colour and there is no detectable electron-spin resonance absorption. This result fits in well with those of Lampe and Noyes [15] and suggests that a cage back-reaction of high efficiency is operating.

Possibly because of such back-reactions, processes which can follow both radical and non-radical paths in the fluid state seem to follow a non-radical path only in rigid media. Examples are ethyl iodide and αα′-azo*iso*butyronitrile. It is not clear whether or not radicals are transiently formed within the solvent cage before the formation of the non-radical products detected.

When radicals are trapped, they are generally found to be derived from the solvent. For example, hydroxyl radicals, which are presumably the first product in the photolysis of hydrogen peroxide, have not been detected; instead, the evidence is strong that they either extract hydrogen from the solvent or add to unsaturated compounds. The mode of interaction occurring when hydrogen peroxide is photolysed in solid acetic or formic acid is still obscure. For acetic acid, there seem to be four possibilities: (*a*) extraction of α-hydrogen to give $\cdot CH_2\cdot CO_2H$; (*b*) attack on carboxylic hydrogen to give $CH_3\cdot CO_2\cdot$; (*c*) addition to give  $CH_3\cdot\underset{\displaystyle O}{\overset{}{C}}(OH)_2$; and (*d*) addition to give $CH_3\cdot\dot{C}(OH)\cdot O\cdot OH$.

Evidence from reactions at room temperature is ambiguous.[10,16] Also, electron-spin resonance results, although they prove conclusively the presence of trapped radicals, do not give an unambiguous identification. The appearance of a violet colour after prolonged irradiation, however, if our postulate be accepted, indicates the presence of the $>\dot{C}\text{–}OH$ group, and hence points strongly to alternative (*d*). If addition to the carboxyl group can occur, one might expect that the direction of addition would be such as to give (*d*) rather than (*c*) since far more delocalisation of the unpaired electron is possible in (*d*), and the hydroxyl radical, being electrophilic, will tend to avoid the positively polarised carboxyl carbon. If such addition occurred at room temperature, it would probably be reversible and not detected.

Nature of the Violet Species.—This problem has been discussed,[5] and it was concluded that, in ethanol, the violet colour was due to the radical $CH_3\cdot\dot{C}H\cdot OH$. These radicals could well have a low-energy transition involving partial charge-transfer between α-carbon and oxygen. However, some recent results [9] cast doubt on this concept so the problem requires further consideration.

All primary and secondary alcohols so far studied become violet after photolysis of dilute solid solutions of hydrogen peroxide, or have a broad band in the 500 mμ region. Tertiary alchols do not develop a band in this region. Irradiation of *tert.*-butyl hydroperoxide or chlorine dioxide in ethanol gives the same colour, but no colour develops when either is irradiated in a mixed hydrocarbon glass. Thus primary or secondary alcohols seem to be necessary ingredients.

Evidence is presented in Part II [17] that primary and secondary alcohols lose α-hydrogen under these conditions. If this is correct, then only when the unit $>\dot{C}\text{–}OH$ is present is a band in the 500 mμ region found.

Alger *et al.*[9] have observed similar colours after high-energy irradiation of solid alcohols. There is one remarkable difference, however: alcohol glasses so coloured are readily

---

[15] Lampe and Noyes, *J. Amer. Chem. Soc.*, 1954, **76**, 2140.
[16] Koltoff and Medalia, *ibid.*, 1949, **71**, 3777.
[17] Part II, following paper.

bleached by visible light whereas our glasses are unaffected. Alger *et al.*[9] obtained very similar electron-spin resonance spectra to ours, and observed no change in these spectra after photo-bleaching. They therefore concluded that the coloured species are *not* the free radicals which give rise to the resonance absorption. The reason for this surprising difference is not understood.

One alternative explanation is that colour-centres are formed, similar to *F*-centres found in ionic crystals. Photolysis of triphenylmethyl-lithium in an E.P.A. glass (*i.e.*, one made from diethyl ether, *iso*pentane, and ethanol) results in photoionisation, but no discrete absorption due to unpaired electrons appeared in the visible region of the spectrum.[4b] Again, our experiments with solutions saturated with lithium chloride strongly suggest that trapped electrons are not the cause of colour, since lithium ions would surely provide good traps for ejected electrons and as a result new colour centres would be formed.

Alternatively, the colour might be due to radical-positive ions remaining after loss of electrons. Such a postulate is reasonable when high-energy radiation is employed, but photo-ionisation is unlikely to be induced by light of 3650 Å wavelength.

We thank Dr. C. H. Bamford and Dr. A. Jenkins for helpful discussion. For this and the following paper we thank Dr. D. J. E. Ingram for help relating to electron-spin resonance measurements, and Courtaulds Ltd. for a grant (to M. G. T.).

DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, SOUTHAMPTON. [*Received, June* 16*th*, 1958.]